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THE

PHYSICAL REVIEW.

THE OPTICAL CONSTANTS OF SODIUM-POTASSIUM ALLOYS.

By Raymond Morgan.

Synopsis.

The optical constants of sodium-potassium alloys were investigated for an entire alloy series by the polarimetric method. Bright metallic surfaces were obtained by filling glass cells with the molten metal in a vacuum. Excepting sodium, all the specimens were observed in the liquid form. In the region near the composition corresponding to NaK the refractivity-concentration curve has a maximum value of 0.137 and the absorptive index-concentration curve has a minimum value of 12.5. *The effect of change in temperature* was studied for some of the mirrors. The solid alloy containing 83 per cent. Na showed a change in the optical constants with a change in temperature, but no change was found for the liquid alloy containing 26 per cent Na. It could not be definitely determined whether the change observed for the solid alloy was due to a change in the optical constants or was due to a possible surface effect resulting from the metal expanding and making better contact with the glass.

THE optical properties of alkali metals have been studied by a number of investigators[1] but as yet no study has been made of the alloys of these metals. Some work has been done on the determination of the optical constants of the alloys of the less oxidizable metals. Binary mixtures of Ag-Te, Ag-Sn, Cd-Hg, Cu-Sn, Cu-Zn and Cu-Ni were studied by Bernouilli.[2] An investigation of the entire alloy series was made for Cu-Ni, Fe-Mn, Ni-Fe, Al-Cu and Cu-Fe by Littleton.[3] Binary alloys of silver with copper and platinum have been studied by Oppitz.[4] Recently Kent[5] has studied bismuth, cadmium, tin, lead, and binary alloys of these. His observations were made on the metals in the molten state. In continuation of the work this paper gives the results of a

[1] Drude, Ann. d. Phys., p. 159, 64, 1898. R. W. and R. C. Duncan, Phys. Rev., 36, 294, 1913. Meese, Gottingen Nachr. Math. Phys. Klasse. Nathanson, (1) Astro. Phys., 44, 137, 1916; (2) Phys. Rev., 11, 227, 1918. Frehafer, Phys. Rev., 15, 110, 1920.

[2] Bernouilli, Zeitschr. f. Elektrochemie, 15, 647, 1909.

[3] Littleton, Phys. Rev., **28**, 306, 1912; **33**, 453, 1912.

[4] Oppitz, Phys. Rev., 10, 156, 1917.

[5] Kent, Phys. Rev., 14, 459, 1919.

determination of the optical constants of sodium-potassium alloys by the polarimetric method.

THE PREPARATION OF THE SURFACE.

Bright metallic surfaces were obtained by filling glass cells (Fig. 1) with the molten metal in a vacuum.[1] Each cell consisted of a cylindrical glass ring 12 mm. in diameter and 8 mm. wide. On the side of the ring was sealed a tube E through which the cell was filled. A fine tube F sealed inside of E helped to prevent metallic oxides from getting into the cell. Plane glass plates were fastened with rock cement on the carefully ground sides of the ring. Only a thin coat of the cement was used and this after being baked at about 140° C. for forty hours was coated with Whiz black engine enamel and again baked.

The melting point curve[2] (Fig. 7) for sodium-potassium alloys shows that at room temperature some of the alloys are solids and some are

Fig. 1.

Fig. 2.

liquids. At present only two investigations have been made upon the effect of the change of state on the optical constants of a metal and the results of these are not in agreement. Data given by Kent[3] for bismuth, lead, cadmium and tin show a difference in the optical properties for the liquid and solid states of these metals. On the other hand it was found by J. J. Haak and K. Sissingh[4] that liquid and solid mercury behave optically in the same way.

In the case of the solid alloys of sodium and potassium special glass cells (Fig. 2) were constructed by means of which observations could be

[1] This method is, in general, the same as used by R. W. and R. C. Duncan in obtaining bright surfaces of sodium and potassium.—PHYS. REV., 36, 294, 1913.

[2] Kurnakow and Puschin, Z. Anorg. Chem., 30, 109, 1902.

[3] Kent, *loc. cit.*

[4] J. J. Haak and K. Sissingh, K. Akad. Amsterdam, 5, 692, 1919.

made on the specimens in both the solid and liquid forms. These cells were made with an internal bulb to which outlet tubes were sealed through the sides of the rim. By passing hot water or steam through the bulb on the interior of the cell the solid metals could be melted. By this method any considerable difference between the results for the mirrors in both the solid and liquid states could easily be detected.

The cells were filled by use of the apparatus shown in Fig. 3. The metal placed in *C* was melted by means of an oil bath. Upon turning *C* in the ground class joint *a* the molten metal would run to the bottom of *A*. The pouring device had the great advantage of getting rid of much of the oxide. The cell was lowered by means of the windlass *B* until the end of the filling tube *E* was well under the surface of the metal. The air now being let in at *D* the metal was pushed into the cell. After the whole apparatus had been allowed to cool, the mirror was taken out and the end of the tube *E* was closed with paraffin. The metal remaining in *C* and *A* was removed with alcohol.

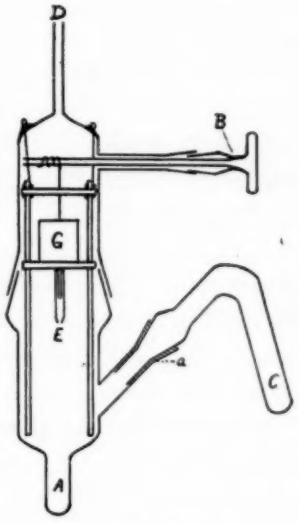

Fig. 3.

Before the tube was lowered into the metal and with the evacuating pumps in operation, the plane glass plates on the sides of the cell were heated in order to drive off occluded gases. The heating was effected by placing the cell in the grid *G* on the sides of which were pieces of mica wound with fine platinum wire. By sending an electric current through the wire it was heated until it was bright red. With the wire thus heated the pumping was continued for about forty-five minutes. After heat treatment the grid was allowed to cool down to a temperature slightly higher than the melting point of the alloy.

The quantities of sodium and potassium to make up an alloy were prepared by cutting off the heavy coats of oxide under paraffin oil. After sponging off the excess oil from the pieces they were placed in known amounts of paraffin oil and weighed. The pieces were then rinsed in gasoline and quickly transferred to *C*. Chemical analyses made of two alloys checked the percentages obtained by the above method to one per cent.[1]

Much difficulty was experienced in obtaining suitable mirrors, there

[1] The writer desires to express his thanks to Mr. R. W. Pfanstiel for assistance in making the chemical analyses.

being many opportunities for failure in the process of preparing the cells and filling them with metal. In all over thirty-five mirrors were made to obtain the ten that were used for the observations. The greatest difficulties were caused by the occurrence of thin oxide films on the surface and by the metal not making good contact with the glass. Excepting the potassium mirror the ones used for investigation were without fault so far as the eye could tell.

Evacuation was accomplished by means of a Gaede molecular pump supported by a Gaede mercury pump in series with a single stage oil pump.

OPTICAL METHOD.

As Drude's method of investigating the optical constants of metals was used throughout this work, it was necessary to observe the values of Δ the phase difference and ψ the azimuth of restored polarization. These were determined by means of a Soleil-Babinet compensator and two nicols mounted on a spectrometer. The nicol used as an analyzer was of the form of the Zehnder half-shadow polarimeter.[1] The settings of the nicol and compensator were made by removing the eye-piece of the telescope and looking directly at the nicol through a small hole placed at the focus of the objective lens in the telescope. A circular field of light was viewed in making the settings. The position of extinction of the analyzing nicol was determined by finding two half-shadow equality positions one on each side of the extinction position.

A Cooper-Hewitt glass tube mercury arc was used as the source of light. The light was separated into its component colors by means of a constant deviation monochromator. The green line 5461 Å. was used. The eye-piece of the monochromator being removed, the beam of green light was allowed to fall on the slit s (Fig. 4) of the collimator of the

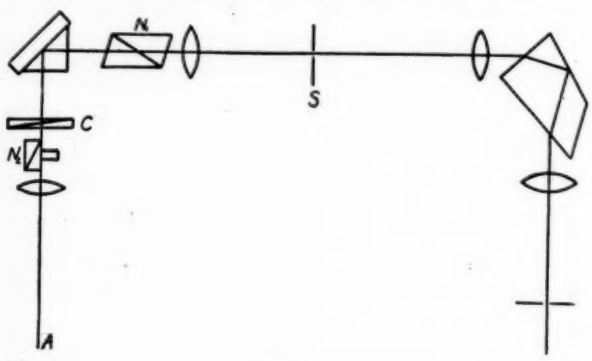

Fig. 4.

[1] Zehnder, Ann. d. Phys., 26 pp. 985, 1908.

spectrometer. The light after passing through the collimator was polarized by the nicol N_1 at an azimuth of 45°.

The mirrors were mounted against the hypotenuse side of a right-angled prism. Either cedar oil or Canada Balsam was placed between the mirror and the prism. One leg of the prism being set normally to the incident light, the light would accordingly strike the metal surface at an angle of 45° and after reflection would pass out normally through the other leg of the prism. The light then passed through the compensator C and the analyzing nicol N_2 and out through the telescope tube A.

The prism used throughout the work was tested for strains by measuring the phase change Δ for internal reflection from the hypotenuse side. The experimental value agreed very closely with the theoretical value as calculated by Drude's equation. Several prisms were examined before one was found that did not give a difference in the two values of Δ.

In the following table is given a summary of the data taken in a particular case for calculating 2ψ. In determining the position of extinction, from 5 to 10 settings of the analyzer for half-shadow equality were made on each side of the extinction position. Accordingly, from 80 to 160 settings of the analyzer were made to obtain one value of 2ψ. The determinations of the phase difference indicated by the compensator are obvious.

TABLE I.

Position of Polarizer.	10° 54′.	190° 54′.	100° 54′.	280° 54′.
Position of analyzer	213° 64.9′ 33° 56.4′	213° 62.2′ 33° 55.4′	305° 17.8′ 125° 18.1′	315° 15.6′ 125° 16.7′
Mean	213° 59.7′		125° 17.0′	
2ψ	88° 42.7′			

RESULTS.

The values of the optical constants were obtained by substitution in the approximative form of Drude's equations as used by R. W. and R. C. Duncan.[1]

The results of the measurements upon a complete series of alloys are given in Table II. With the exception of sodium it is believed that the values obtained for n (index of refraction) and k (index of absorption) are within 10 per cent. of the actual values. The reflecting power R

[1] R. W. and R. C. Duncan, loc. cit.

was calculated from the mean value of n and k. The specimens were all in the liquid state excepting sodium and in one case potassium. From other data subsequently given, it is probable that there is not a wide variation between the constants for the solid and liquid states. The index of refraction from air to metal is that given in every case.

The results are shown graphically in Figs. 5 and 6. No attempt was made to determine the detailed form of the curves as this would have required measurements on a very large number of mirrors. The curves show, however, that in the region near the eutectic points the index of refraction reaches a maximum and the index of absorption becomes a minimum. The variations of the optical properties of the alloys with the concentration are therefore in the opposite sense from

TABLE II.

Mirror No.	Per Cent. of Potassium by Weight.	Atomic Per Cent. of Potassium.	2ψ.	Δ.	n.	k.	Mean n.	Mean k.	R.
1	0	0	89° 20.9′	131.3°	.041	52.5			
2			89° 14.2′	131.4°	.047	46.1	.047	47.3	96.9
3			89° 18.3′	133.8°	.047	48.7			
3			89° 11.6′	132.7°	.053	42.1			
1	17.3	11.0	88° 42.7′	132.4°	.083	26.4	.081	27.2	94.6
1			88° 47.0′	132.5°	.079	28.0			
1	36.2	25.1	88° 9.5′	126.4°	.100	18.5	.100	18.5	91.4
1	45.0	32.5	87° 58.0′	125.5°	.108	16.9	.108	16.8	90.4
1			87° 58.2′	125.6°	.108	16.8			
1	55	41.8	87° 51.3′	125.1°	.113	15.9	.115	15.6	89.7
1			87° 47.0′	125.5°	.117	15.4			
1	66	53.3	87° 23.0′	124.5°	.135	12.9			
2			87° 14.3′	122.7°	.137	12.1	.137	12.5	87.0
2			87° 14.3′	123.3°	.139	12.5			
1	74.2	62.7	87° 25.2′	122.7°	.128	13.0			
2			87° 19.4′	122.5°	.132	12.5	.124	12.8	86.9
1			87° 27.4′	119.8°	.119	12.9			
1			87° 27.5′	119.9°	.118	12.9			
	84.3	76	88° 7.5′	120.3°	.088	17.6	.088	17.6	90.2
1	100	100	88° 39.0′	119.5°	.062	19.3	.060	21.5	91.4
1			88° 40.8′	115.8°	.057	23.6			

those found by Oppitz[1] for the optical constants of silver-copper alloys. In the case of the alloy series of Al-Cu, Cu-Ni, and Cu-Fe, Littleton[2] found that the indices of refraction increased to a value higher than that of either component forming the series and the index of absorption became a minimum at about the same concentration. This is similar to the results for sodium-potassium alloys.

TEMPERATURE EFFECTS.

In some cases when the mirrors were heated in order to convert the metal into the liquid state, considerable changes of the optical constants were noted with changes in the temperature. A number of observations were accordingly made in order to determine more closely the effect of changing the temperature upon the optical constants.

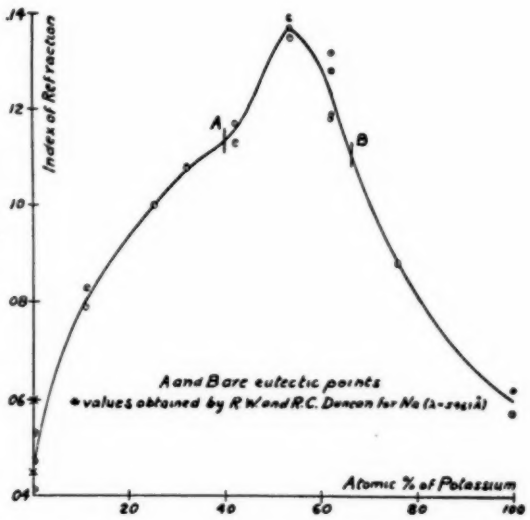

Fig. 5.

82.7 per cent. sodium and 17.3 per cent. potassium.—The results for this alloy are given in Table III. and a graphical representation of the probable variation of the refractive index with temperature is given in Fig. 8. The change in the optical constants in raising the temperature from 75° C. to 100° C. was less than the experimental error.

Sodium.—In making the measurements on the sodium mirror the field as viewed in setting the analyzer and compensator became distorted, a light circular band appearing on one side of the field. The

[1] Oppitz, loc. cit.

[2] Littleton, loc. cit.

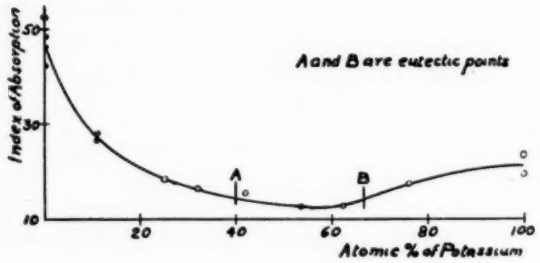

Fig. 6.

distortion was first noticeable at a temperature of about 60° C. and was quite marked at 100° C. It was also noted that the two positions of the analyzer for one setting of the polarizer lacked as much as 40′ of being 180° apart. Fairly consistent results showing a change in the optical constants were obtained for temperatures of 26°, 60° and 100° C., but they are not considered as reliable.

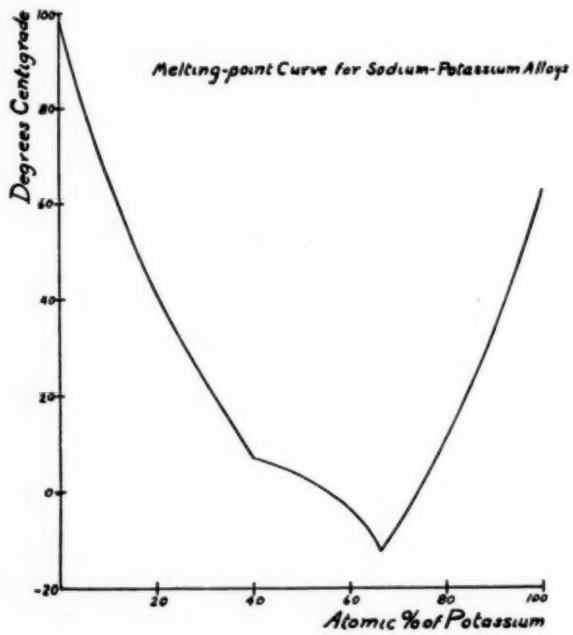

Fig. 7.

It is most probable that the strains present in the sodium mirror were produced in the cover glasses by the unequal expansion of the cylindrical wall of the cell. The small ring with the three tubes sealed to it was a very complicated piece of glass blowing and would be likely

to be under such high tension that when heated it would expand unequally and produce strain in the cover glasses. A few empty cells were examined for such strains. The method of examination consisted in mounting the right-angled prism with its hypotenuse side against an empty cell so that the light was totally reflected from the back surface of the cover glass, and measuring the phase change Δ when water at 15° C. and later steam at 100° C. were passed through the bulb in the cell. The greatest variation in Δ found for the two temperatures was a little less than two degrees. In this case the field viewed in making the analyzer and polarizer settings was slightly distorted. The cell that contained the alloy, 82.7 per cent. sodium and 17.3 per cent. potassium, showed no variation at all.

Potassium.—Table IV. In order to make the observations on potassium, the mirror had to be heated so as to free the surface of the irregularities due to the contraction of the metal from the glass. At a temperature of 54° C. the surface irregularities were found to disappear and the field as viewed in making the settings of the analyzer and compensator became of uniform intensity.

25.8 per cent. sodium and 74.2 per cent. potassium.—Table V. As this mirror did not contain a heating bulb the heating was effected by means of fine platinum wire wound on mica. Sufficiently accurate values of

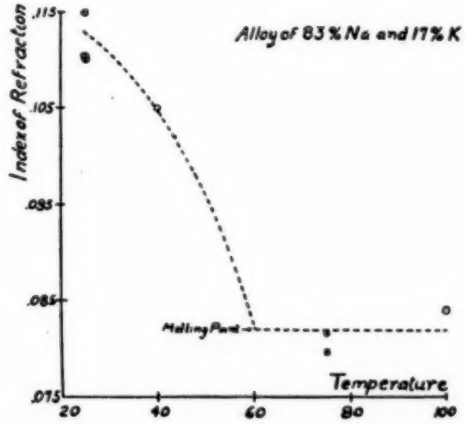

Fig. 8.

the temperatures were obtained by taking a mercury mirror of the same size and shape as the above mirror, mounting it under exactly the same conditions and by means of a small mercury thermometer inserted in the mirror noting the temperature for different values of the current. The variations in the values of n and k are within the limits of experimental error.

TABLE III.

82.7 Per Cent. Sodium and 17.3 Per Cent. Potassium.

Date of Observation.	Temperature.	2ψ.	Δ.	n.	k.
11/22/21.....	Room 27°	88° 4.9′	130°	.115	17.9
11/24/21.....	75°	88° 42.7′	132.4°	.083	26.4
11/25/21.....	Room (24°)	88° 1.1′	128.7°	.115	17.3
11/27/21.....	40°	88° 15.2′	130.3°	.105	19.6
2/ 3/22.....	25°	88° 6′	129°	.111	18.0
2/ 4/22.....	74°	88° 47′	132.5°	.079	27.9
2/ 5/22.....	100°	88° 44′	133°	.084	26.8
2/ 6/22.....	25°	88° 7′	128.5°	.110	17.7

TABLE IV.

Potassium.

Date of Observation.	Temperature.	2ψ.	Δ.	n.	k.
1/7/22.....	54°	88° 39′	119° 30′	.062	19.3
1/9/22.....	73°	88° 40.8′	115° 8′	.057	23.6

TABLE V.

25.8 Per Cent. Sodium and 74.2 Per Cent. Potassium.

Date of Observation.	Temperature.	2ψ.	Δ.	n.	k.
9/11/21.....	Room	87° 25.2′	122.7°	.128	13.0
9/17/21.....	"	87° 19.4′	122.5°	.132	12.5
1/29/22.....	" (25° C.)	87° 27.4′	119.8°	.119	12.9
1/30/22.....	47°	87° 27.4′	119.8°	.119	12.9
2/ 1/22.....	65°	87° 28′	119.4°	.117	12.9
2/ 2/22.....	Room (25°)	87° 27.5′	119.9°	.118	12.9

Results given in Tables III., V., and Fig. 8, would indicate that the optical constants of the liquid alloys remain constant for the given ranges of temperature. In the case of the solid alloy (Table III. and Fig. 8) there is a very marked change in n and k resulting from the change in temperature and the process of fusion. However, from a consideration of the potassium mirror where heating was necessary to obtain a smooth surface and where the change in the optical properties for a change in state were within the limits of experimental error, it would be impossible to tell whether the changes found for n and k for the above solid alloy were actually due to a change in the optical properties, or were due to a surface effect. There may have been slight irregularities in the surface

produced by the contraction of the metal from the glass which could not be detected by the eye, but which would cause an error in the observed values of 2ψ and Δ. It is possible that such a surface effect may be the cause for the difference in the results obtained for two potassium mirrors by R. W. and R. C. Duncan.[1] The difference between the results of Meese[2] and those of R. W. and R. C. Duncan for sodium and potassium may also be due to such an effect.

It is proposed to continue this work by making a more detailed study of the effect of the change of temperature upon the optical properties of sodium and potassium and perhaps some of the alloys.

In conclusion the writer wishes to acknowledge his indebtedness to Professor H. C. Richards for having suggested this problem and for his many valuable suggestions throughout the investigation.

RANDAL MORGAN LABORATORY OF PHYSICS,
UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, PA.

[1] R. W. and R. C. Duncan, loc. cit.

[2] Meese, loc. cit.

RELATIVE INTENSITIES OF STARK EFFECT COMPONENTS IN THE HELIUM SPECTRUM.

BY JOHN STUART FOSTER.

SYNOPSIS.

Modified Lo Surdo tube for observing the Stark effect.—By placing the tube with its axis perpendicular to the slit and using the cross-section of the cathode afflux where the field is a maximum, separate and parallel components were obtained. Pitting of the aluminum cathode, however, causes a gradual shifting of the field and consequent blurring of the components with exposures of several hours, and this limits the usefulness of the method at present.

Relative intensities of the Stark effect components of the helium lines λλ *4922, 4472, and 4388 Å in a field of 15,000 volts/cm.*—Spectrograms were taken of the *p* and *s* components in turn through a neutral wedge, using a five-prism spectrograph (Figs. 3–5); then energy distribution curves were calculated from the contour of the images and the corresponding wedge densities (Fig. 6), and the relative intensities were obtained by integration. The results for the main *p* components follow in order of increasing wave-length: for the line 4388, 8.2 (isolated), 4.1, 19.2, 28.0; for 4472, 168, 694; for 4922, 9.7, 31.6. Corresponding results for the *s* components are: for 4388, 1.0 (isolated), 3.0, 11.3, 9.5; for 4472, 76, 464; for 4922, 6.2, 21.4.

INTRODUCTION.

IT is the purpose of the present paper to describe a new method for the observation of the Stark effect, and its application to the determination of relative intensities of components of lines in the helium spectrum.

As is well known, there are two distinctly different types of discharge tubes which have been commonly employed in the study of the Stark effect. (*a*) Stark[1] and his fellow workers have used, initially, the canal-ray tube in which the canal rays upon passing through the perforated cathode enter a uniform field between the cathode and an auxiliary electrode. The light is not intense; certain lines do not appear (notably Fowler's enhanced helium series beginning with λ 4686, of theoretical interest); but the method has a very great advantage in that the field strength is known directly. It has been customary to use two current sources, one of which must supply direct current. The components appear separate and parallel on the plate. (*b*) Lo Surdo[2] first used the method employing the electric field in the cathode fall. A variety of tubes of the Lo Surdo type have been used and the field distribution

[1] J. Stark, Elektrische Spektralanalyse chemischer Atome, Leipzig, S. Hirzel, 1914.

[2] A. Lo Surdo, Rendiconti d. Lincei, **22**, 664, 1913.

changes with the tube design. The light from the center of the stream immediately in front of the cathode in a tube of small diameter is more intense than that from a canal-ray tube, and Fowler's series is present. Field strengths are found indirectly through the separation of well-known components, which have been carefully studied in the canal-ray tube. In all previous investigations the axis of the tube has been parallel to the slit of the spectrograph so that, due to the variable field, the components appeared on the plate as curved lines.

The writer has undertaken the problem of finding the relative intensities of Stark effect components by means of a neutral wedge.[1] Obviously the canal-ray tube might have been used, though it supplies a relatively weak source. It should prove satisfactory for intensity measurements in the Balmer series, and elsewhere of less immediate theoretical interest. At the time this work was started, however, this tube had not been used with a single source of current[2] and as two satisfactory sources were not available it was decided to use a Lo Surdo tube with helium as the gas. The usual source of light in the latter tube consists of a thin section cutting through the center of the stream; and includes not only the bright central portion, but an equally thick part of the less intense outer portion. The resulting spectrograms show well-defined components which fact indicates that in a cross-section of the stream at any point the field is effectively constant or nearly so.

If the field throughout the cross-section be constant or nearly constant, either actually or effectively, then the main components of a line should be separate and parallel if the tube be used with its axis perpendicular to the slit. It thus appears to be possible to obtain with a Lo Surdo tube components which have the same appearance on the plate as those from a canal-ray tube. The neutral wedge method for intensity measurement is equally applicable, and there are the advantages of more light and more lines.

The form of tube first described by Nyquist[3] was selected as a good one with which to start the investigation. In this tube the field distribution is such that there is a maximum value so that for a short distance along the axis of the tube the field is nearly constant. If the image of this section of the source be allowed to drift across the slit during an exposure, then the blurring of the components, due to cathode pitting, will be a minimum.

[1] J. W. Nicholson and T. R. Merton, Phil. Trans., Ser. A, **216**, 459, 1916.
[2] F. Tuczek and W. Heuck, Ann. d. Phys., **63**, 766, 1920.
[3] H. Nyquist, PHYS. REV., **10**, 226, 1917.

The reader is referred to the original paper by Nicholson and Merton[1] for the theory of the wedge. The relative energy content of two components is given by

$$\frac{\int I_{\lambda_1} d\lambda_1}{\int I_{\lambda_2} d\lambda_2}$$

where the subscripts refer to the components. I_λ is the intensity of monochromatic light of wave-length λ which has just penetrated the first surface of the wedge. The above may be written

$$\frac{\int \log_{10}{}^{-1} \frac{h_{\lambda_1} D_\lambda}{M} d\lambda_1}{\int \log_{10}{}^{-1} \frac{h_{\lambda_2} D_\lambda}{M} d\lambda_2},$$

where $\log_{10}{}^{-1}(h_\lambda D_\lambda / M)$ is defined as the photographic intensity of light of wave-length λ. The height h_λ of a component varies over its width in accordance with the distribution of energy and is measured on an enlargement of magnification M. D_λ is the change in the density of the wedge per millimeter of its length, for light of wave-length λ. It may be assumed constant over the region including the components of any one line herein investigated. The dispersion of the spectrograph, too, is similarly constant. Thus it is easy to construct energy distribution curves for the components of a line, from the contour of the enlarged images and the corresponding wedge densities. From such curves the relative intensities of the components may be found by means of a planimeter.

EXPERIMENTAL.

The helium, prepared from thorianite and initially at atmospheric pressure, is kept in a bulb which is attached to the main vacuum apparatus by a tube in which there is a stopcock and a constriction. Thus the gas can be admitted to the vacuum in any desired quantity. The arrangement is such that it can be forced around a circuit, and a charcoal bulb immersed in liquid air is used to keep it pure. A transfer pump helps to circulate the gas and to regulate the pressure in the discharge tube. A ballast capacity of three liters tends to keep the pressure constant.

The discharge tube is of pyrex glass, and is shown in Fig. 1. It consists of a main portion M, of 1.3 cm. internal diameter, which supports the aluminium anode A; and an auxiliary tube B, which insulates the greater part of the cathode rod C. The two glass parts B and M are

[1] Loc. cit.

sealed together with hard wax. The cathode is an aluminium rod 3.5 mm. in diameter; and is supplied with two collars, which fit B as closely as possible. It is held in position by a coiled steel spring, which presses one of the collars against the surrounding tube at a point where the latter is purposely dented. The space between the rod and the glass wall is 0.5 mm. wide. Between the glass tubes M and B, and fitted closely to each, is a hollow cylinder of aluminium D. A small portion of this is in the form of a thin-walled tube and lies inside B. This part of D has an internal diameter of 3 mm., ends 7 mm. from the cathode surface, and does not touch the glass walls. The side tube S_3 is placed opposite the cathode surface and is 4 cm. long. The window W is sealed to this tube with wax. Narrow slits are made through B and D. The side tubes S_1 and S_2 form a part of the circuit around which the helium may be forced. The useful life of a tube of this type is about sixty hours.

The discharge is very stable. It is necessary, however, to have constant communication with the charcoal bulb. In one half hour from the time the tube is started, it is possible to increase the pressure to 3 mm. of mercury with safety. During this time a pit in the cathode is started. This pit apparently grows as long as the tube lasts. In a tube 60 hours old it is 2.8 mm. deep and the diameter is exactly equal to that of the aluminium tube close to the cathode. The greater part of the pit is uniform in diameter. The bottom is conical. The tube may be run without any cooling device, provided the current does not exceed 3 mil. amps. During an exposure of 7 hours no change could be detected in the voltage or current. In the longest exposure (18 hours) there were a few slight fluctuations. Corrections were immediately made by adjustment of the ice-cooled water resistance or the pressure of the helium. The variation was never more than one per cent. of the total. It follows that the variation in the field to which the source is subjected, which comes as a result of irregularity in the discharge, is no greater than that due to ripples in the rectified current, and is less than that caused by the drift and redistribution of electric field which accompanies the pitting of the cathode.

The source of direct current is essentially that described by Nyquist.[1]

Immediately in front of the window of the discharge tube is a Bausch and Lomb Tessar lens of 5 cm. focal length and 1.2 cm. aperture. A double-image prism, placed close to the lens, separates the images, which are double the size of the source. At the focal plane a diaphragm stops one of the images. A sphero-cylindrical lens is so placed that the

[1] Loc. cit.

images formed by the Tessar lens are in the principal plane of the spherical portion the focal length of which is 7.5 cm. The light is focused on the slit by the cylindrical portion of 15 cm. focal length. On the cylindrical surface is a diaphragm with a square opening 5.6 mm. on each side. This is just filled with light by the Tessar lens.

The wedge is of dense neutral glass supplied and ground by Brashear. At the thick end it is very dark, though not visually opaque to daylight. The neutral glass is cemented to a wedge of colorless glass such that the two pieces form a plane parallel plate. The colorless glass extends beyond and protects the knife edge of the neutral glass. The wedge is mounted on a slide immediately in front of the slit. The opening in the slide is 5 mm. long. One end of this opening matches the thin end of the wedge.

The collimator and camera lenses are doublets of 45″ focal length and 3″ aperture. They were designed by Professor Hastings and ground by Brashear from glass especially transparent to light in the visible region.

The dispersive apparatus consists of five glass prisms with circular faces 6 cm. in diameter. They are on a base of cast iron which is accurately flat. The dispersion is 4.0 Å./mm. at λ 4472.

RESULTS.

The lines λ 4922, 4472, and 4388 were examined. Of these, 4922 and 4388 are the second and third terms respectively of the second subordinate series of parhelium.[1] The first term is 6678. The line 4472 is the second term of the diffuse series in the system of pairs. The first three members of this series are λ 5876, 4472, and 4026.

Seed 30 plates were used. The even illumination of the slit is shown in Fig. 2. On the negative from which this figure is taken one can clearly see the "isolated component" of 4922, observed by many investigators, and classified by Liebert[2] as the first term of the "new" third subordinate series. This line is weak, and does not show on the plates taken with the wedge in position. The "isolated component" of 4388, the second term of the above-mentioned new series, is caught at a point where, as the wedge spectrogram shows more clearly, it is beginning to break into the two components observed by Nyquist and by Takamine and Kokubu.[3]

After making sure of even illumination of the slit, the wedge was placed in position and an exposure of seven hours was made. The resulting plate, No. 12, is the one from which all measurements of the

[1] F. A. Saunders, Astrophys. Journ., **50**, 151, 1919.

[2] G. Liebert, Ann. d. Phys., **56**, 610, 1918.

[3] T. Takamine and N. Kokubu, Mem. Coll. of Sci., Kyoto, **3**, 275, 1919.

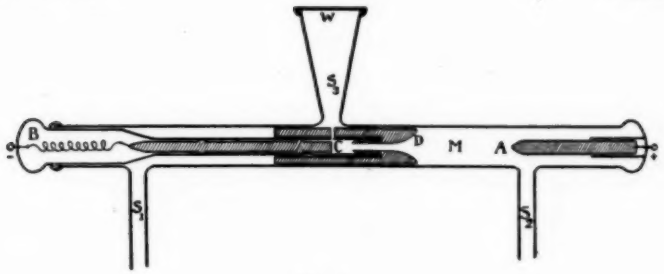

Fig. 1.

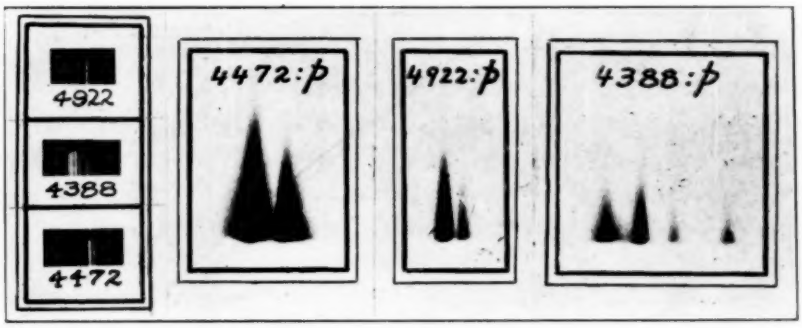

Fig. 2. Fig. 3. Fig. 4. Fig. 5.

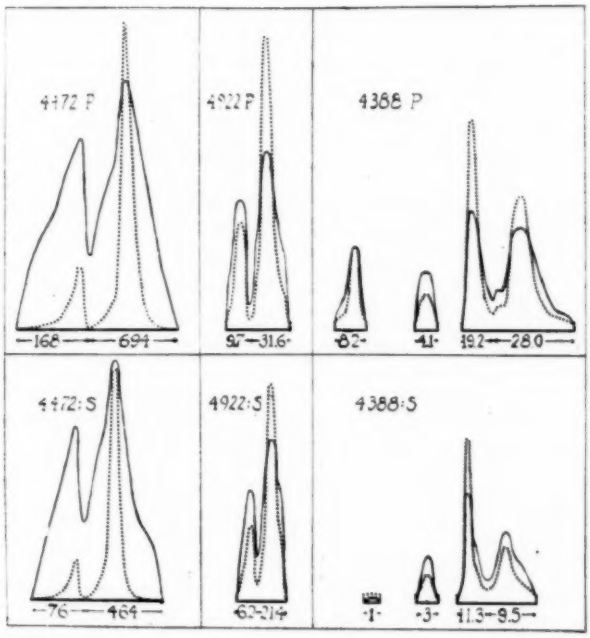

Fig. 6.

J. S. FOSTER.

p components are taken. It is thought to be reliable, because no change was detected in the voltage or current during the exposure. The voltage on the tube was 6000 v.; the current 3 mil. amp.; and the pressure of the helium was 2.8 mm. Figs. 3 and 4 are enlargements of the images of 4472 and 4922 respectively, and are taken from plate No. 12. Fig. 5 is an enlargement of 4388 and is taken from a plate exposed for a longer period. The s components are taken from a plate exposed for eight hours under conditions similar to those under which No. 12 was obtained. The field strength is found from the separation of the main components of 4472.

The continuous lines of Fig. 6 represent the contours of all lines examined. As the background of the plate was quite clear, the enlargements were sketched directly, through the aid of an instrument commonly used by biologists for the sketching of slides. The distortion was small and the error arising therefrom is considered less than that due to imperfectly judging a contour of constant density. The latter operation involves an error of about one per cent.

It is, of course, evident that the unit used herein for intensity measurements is that intensity which under the photographic conditions produces an effect on the plate, which is just visible. Therein lies a great advantage of the wedge method, for the investigator need know nothing about the behavior of the plate toward the various frequencies and intensities of light; and encounters no difficulties due to irradiation. In order to draw the energy distribution curves for a group of components, one needs to know the following quantities only: (i) D_λ, the change in wedge density per millimeter length of wedge, for the average frequency of light involved; (ii) a series of values of h_λ, the height of the image, at various points over the widths of the components; and (iii) M, the magnification of the enlargement on which the heights are conveniently measured. The ratio h_λ/M gives, so far as we can detect, the length of wedge penetrated. The physical meaning of D_λ is seen from the following consideration. Let two constant sources of monochromatic light of wave-length λ_0 and of intensities $A > B$ be such that, for otherwise identical photographic conditions, the length of wedge penetrated by the light of intensity A exceeds by *one millimeter* the length penetrated by the light of intensity B; then $\log_{10} A/B = D_{\lambda_0}$.

Because the energy distribution quite clearly varies with the components, at least under ordinary conditions of electric field, dispersion, and resolution, the heights[1] of the components are inadequate for the accurate determination of relative intensities. If, however, the heights

[1] J. W. Nicholson and T. R. Merton, loc. cit.; also Phil. Trans., *A.*, **217**, 231, 1917.

be measured at a large number of points over the width of each component or group of unresolved components, and be used, together with the wedge density, to plot the distribution curves; then a much closer approximation is obtained. This has been done. The dotted lines in Fig. 6 represent the energy distribution. Under each main component will be found the relative energy content which has been assigned to it. There remains, nevertheless, an error which is at present hard to evaluate. This is due mainly to a variation of the field, which variation affects the position of each real component to a degree dependent upon the distance from the original line. Thus the outside components are the most blurred.

The usefulness of the present method is limited, therefore, by the cathode pitting which produces the effect just mentioned. Unless conditions be changed, longer exposures will be required to obtain measurements of Fowler's series, and longer exposures will produce a blurring which may seriously affect the accuracy. Nevertheless, it is well known that the Lo Surdo method has led to the discovery of new lines, in fact new series of lines, with exposures which under ordinary conditions of spectrographic apparatus were for periods of a few hours. Also the writer has observed that in an aged horizontal tube the analysis obtained with short exposures is apparently quite equal to that produced by means of a canal-ray tube. It has seemed worth while, therefore, to investigate further the possibilities of the method herein outlined. A design of tube which will reduce or eliminate the cathode pitting seems the most probable way out of the difficulty.

The extension of the investigation has been made possible by the National Research Council.

The writer wishes to express here his deep indebtedness to the late Professor Henry Andrews Bumstead, who proposed the problem, devised the method of attack, and gave direction and encouragement during the first part of the work. He desires also to extend his best thanks to Professor Leigh Page for his interest and direction. His thanks are further due to Professor H. S. Uhler, whose exact information and advice regarding spectroscopic apparatus have removed many difficulties.

SLOANE LABORATORY,
YALE UNIVERSITY,
April, 1922.

QUENCHING: A MATHEMATICAL STUDY OF VARIOUS HYPOTHESES ON RAPID COOLING.

By K. Heindlhofer.

Synopsis.

Mathematical Study of the Temperature Changes in a Hot Body after Quenching, Assuming Various Conditions of Heat Flow from the Surface.—(1) Assuming no thermal resistance at the surface, theoretical cooling curves for a steel ball and a steel plate are computed (Fig. 1). (2) Assuming constant thermal resistance, the general equation is derived for the case of a cylinder of finite length (Eq. 17). (3) Assuming a vapor layer which conducts the heat to a liquid layer at rest, the general solutions for the temperatures at the surface of a large body (Eq. 41) and of a plate (Fig. 5) are obtained. (4) Assuming that the heat after passing through the vapor layer is carried away by convection at a uniform rate, the equation and curves are obtained for the case of a plate (Eq. 58; Fig. 6).

Heat Flow from a Metal Cylinder Quenched in Water.—By comparing various experimental cooling curves with the theoretical curves obtained above, it is evident that after the first stage of quenching none of the assumed conditions correspond to the facts. It is found that the rate of transfer of heat through the surface is not constant but is an exponential function of the temperature of the surface. Smaller cylinders seem to have less specific heat flow. The discrepancy with theory is doubtless due to the neglect of the bubbling which begins almost immediately.

Reheating of the surface of a body immediately after quenching, due to sudden formation of a steam jacket, does not occur. Reheating as evidenced by structural investigation may occur in a later phase of quenching.

I. Hypothesis No. 1.

Sudden cooling of the surface to final temperature.

This hypothesis has been dealt with by Fourier.[1] It presupposes a quenching medium, the cooling effect of which is infinitely rapid. The cooling of the solid depends then entirely on its thermal and geometrical properties.

The conclusions which are derived from this hypothesis are of value in certain cases. A body with high specific heat capacity and low conductivity will evidently be cooled very rapidly at the surface. Another case where this hypothesis is effective is the central portion of a large body, which is very little depending on the quenching medium. This may be clear when it is considered that after the surface has cooled, the flow of heat to the surface will rapidly diminish on account of the thick layer interposed between the hot interior and the cold surface. This will be proven in the next section.

On the other hand, the temperature in small bodies of high diffusivity is inaccurately represented by this hypothesis. The inaccuracy is greatest at the surface itself.

The hypothesis under consideration represents the extreme, the ideal which may be approached, more or less. If applied to the sphere, the temperature distribution is as follows:

$$(1) \qquad \frac{u - u_0}{u_i - u_0} = \frac{2R}{\pi\rho} \sum_{m=1}^{\infty} (-1)^{m+1} \frac{1}{m} e^{-m^2 a^2 (\pi/R)^2 t} \cdot \sin\left(m\pi \frac{\rho}{R}\right),$$

u_i initial temperature (assumed to be uniform at time $t = 0$),
u temperature at the radius ρ,
u_0 final temperature or temperature of the quenching medium,
ρ variable radius,
R radius of the sphere,
t time,
a^2 diffusivity. For steel we assume $a^2 = 0.111$ cm.^{2}/sec.

The corresponding equation for the center of an infinite slab is

$$(2) \qquad \frac{u - u_0}{u_i - u_0} = \frac{4}{\pi} \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{2m - 1} e^{-(2m-1)^2 a^2 (\pi/2l)^2 t},$$

where l is half the thickness of the slab.

Figs. 1*a* and 1*b* and the three-dimensional model Fig. 1*c* shows temperature distribution in a steel ball of 1 cm. radius, assuming fastest

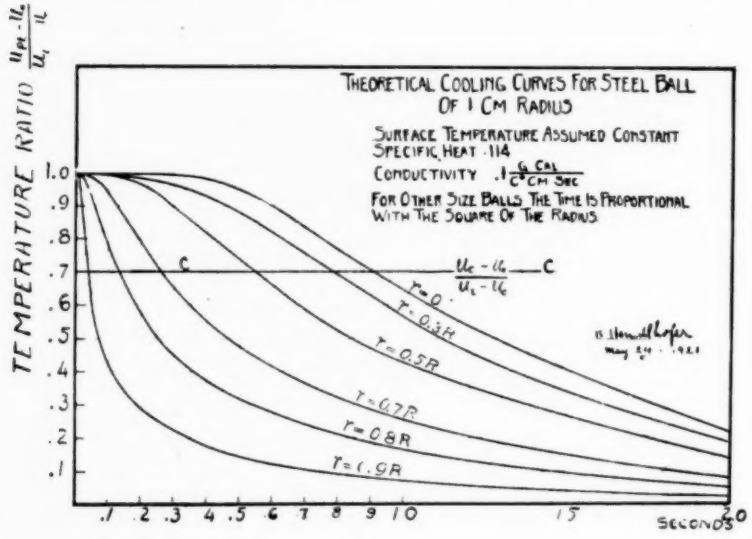

Fig. 1*a*.

possible quenching, *i.e.*, given by equation (1). The values shown in Fig. 1 may be used to determine the temperature in any sphere with any thermal constants as the exponent in equation (1) remains unchanged

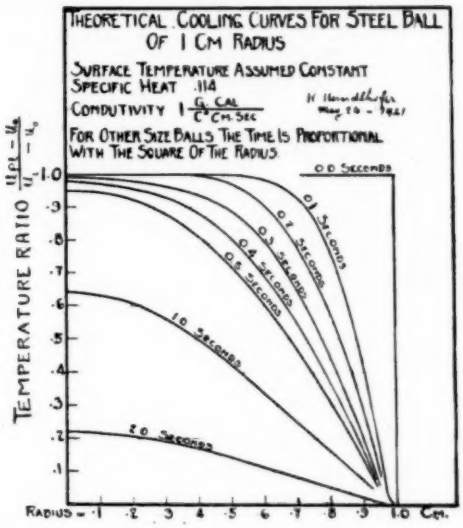

Fig. 1*b*.

if t is increased in the same proportion as R^2 and inversely as a^2. From this it is obvious that in order to derive new diagrams from the old one for other values of R and a^2, it is only necessary to change the abscissa scale to suit.

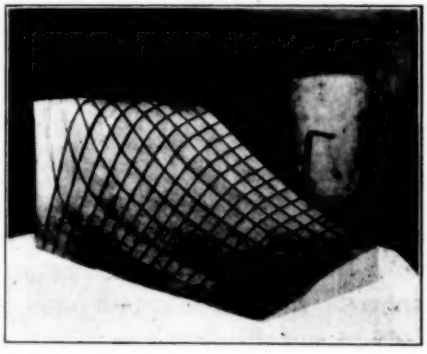

Fig. 1*c*.

Fig. 1*d* shows the curves of Fig. 1*a* on semi-logarithmic paper. Equation (2) is plotted in Fig. 2. The steady flow condition in this case appears as a straight line and the slope of the lines representing temperature-time in various depths, is the same. Thus the logarithmic plotting has the advantage of simplicity, furthermore, it is valuable in deciding whether an experimental cooling curve follows the exponential law.

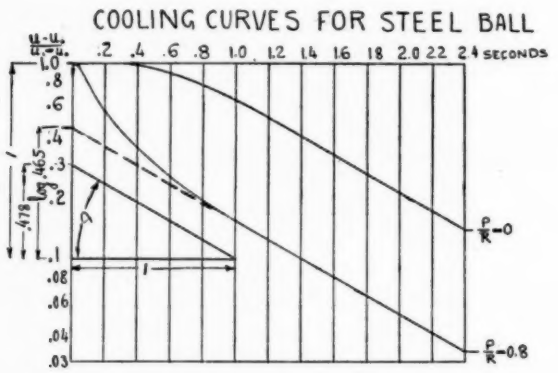

Fig. 1*d*.

Fig. 1*a* may be useful to demonstrate the effect of over-heating of steel on its ultimate hardness. It has been shown[2] that the quenching speed of steel through the transformation range, is the determining factor for the resulting hardness. There is a critical cooling speed, below which soft structure with more or less troostite is formed and above which hard structure with pure martensite or martensite plus austenite, is produced. Thus the slope of the curves at the transformation range is of interest.

The ordinates in Fig. 1*a* are expressed in relative units. As the total temperature drop is chosen for unit, all other temperatures will be expressed in fractions of this unit. In order to see the influence on the speed of cooling by raising the quenching temperature to higher values, it is not necessary to replot the curve, but it is sufficient to drop the line *CC*. The slope of the temperature-time curve at the intersection with *CC*, represents the cooling speed at the corresponding point. An inspection of the curve shows that an initial temperature only slightly above the transformation point cannot result in rapid cooling through the transformation range. This is especially true for points in the vicinity of the center of the sphere. In order to obtain rapid cooling, the quenching temperature should be sufficiently above critical. This is in accordance with experience.

II. Hypothesis No. 2.

Heat emitted by a unit area in a unit time is proportional to the difference between the surface temperature and the temperature of the quenching liquid (Newton's cooling law). This is equivalent to assuming a constant surface resistance.

Newton's cooling law, *i.e.*, law of surface emission of heat which does not assume instantaneous cooling of surface, may be written

$$(3) \qquad -K\left(\frac{\partial u}{\partial x}\right)_s = H(u_s - u_0),$$

where K = conductivity of the metal,
H = constant surface cooling,
u_s = variable surface temperature,
u_0 = temperature of the quenching liquid at a great distance from the quenched body. u_0 is assumed to be constant.
S indicates surface.

Equation (3) may be interpreted in two ways, viz.:

(*a*) The amount of heat emitted by a unit area in a unit time is proportional to the difference between the surface temperature and the temperature of the surrounding medium.

(*b*) Imagine an insulating layer on the surface. Let the temperature on the two sides of this layer be u_s and u_0. Let the thickness of the layer be "d" and assume d small, *i.e.*, the heat capacity negligible. Its conductivity should be low enough to have appreciable effects in spite of the small thickness. According to the fundamental conception of heat conduction

$$-K'\frac{u_0 - u_s}{d} = -K\left(\frac{\partial u}{\partial x}\right)_s.$$

If K'/d be set equal to H, equation (3) is obtained, which proves that *Newton's cooling law may also be interpreted as a constant surface resistance obstructing emission of heat.*

The problem of heat flow under the assumption of equation (3) was solved by Fourier and Poisson for the sphere, the slab, the prism, the cube, and the infinite cylinder.

In order to compare the two types of coolings defined by Hypotheses 1 and 2 respectively, consider the cooling equation for an infinite plate as given by Poisson:

$$(4) \qquad \frac{u-u_0}{u_i-u_0} = \sum_{m=1}^{\infty} e^{\alpha^2\lambda_m^2 t} \cdot \left[\frac{\lambda_m \cos(x+l)\lambda_m + \frac{H}{K}\sin(x+l)\lambda_m}{\frac{H}{K} + l\left(\frac{H^2}{K^2} + \lambda_m^2\right)}\right]\left[\sin(\lambda_m 2l) + \frac{H}{K\lambda_m}(1 - \cos\lambda_m 2l)\right],$$

$$(5) \qquad tg(\lambda_m l) = \frac{H}{K}\frac{l}{\lambda_m l}, \qquad (6) \qquad tg(\lambda_m l) = -\frac{\lambda_m l}{l}\cdot\frac{K}{H}.$$

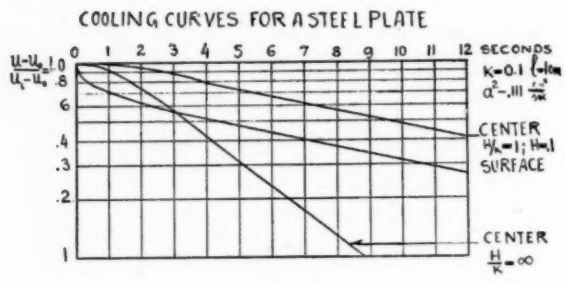

Fig. 2.

Equation (4) is plotted on Fig. 2 for a steel plate, 2 cm. thick with a diffusivity $a^2 = 0.111$ and $H = 0.1$.

The extreme cases of great surface emissivity on the one hand and great thickness of the plate on the other, are of interest. For these cases either H/K or l approach infinity and equation (5) becomes

$$\lambda_m l = (2m - 1)\frac{\pi}{2}.$$

Substituting this into equation (4) the latter becomes for $x = 0$ the same as equation (2), which proves the statement made in the second paragraph of Section 1, that in case of large bodies the cooling at the center does not depend much on the value of the surface emissivity H/K as long as H/K is not too small. *In practice this would mean that quenching speed cannot be improved at the center of a bulky piece of metal by substituting water in place of oil.*

Due to the fact that a great number of quenching experiments were conducted on cylinders the height of which is comparable with their diameter, the solution for the cylinder of finite length is important. In order to solve it, let us make Fourier's equation in cylinder coördinates, our starting point.

$$\frac{\partial u}{\partial t} = a^2\left(\frac{\partial^2 u}{\partial \rho^2} - \frac{1}{\rho}\frac{\partial u}{\partial \rho} - \frac{\partial^2 u}{\partial z^2}\right). \tag{7}$$

This equation is satisfied by the particular solution:

$$u = xe^{-mt}\cos pz, \tag{8}$$

where x is a new variable depending on ρ only. Substitute (8) in (7)

$$\frac{\partial^2 x}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial x}{\partial \rho} + \left(\frac{m}{a^2} - p^2\right)x = 0. \tag{9}$$

This is the differential equation of the Bessel functions. The solution is

$$x = J_0\left(\rho\sqrt{\frac{m}{a^2} - p^2}\right). \tag{10}$$

Therefore the particular solution (8) becomes

$$u = J_0\left(\rho\sqrt{\frac{m}{a^2} - p^2}\right)e^{-mt}\cos pz. \tag{11}$$

At the curved surface $\rho = R$ Newton's cooling law (eq. 3) should be satisfied by (11).

$$H(u)_{\rho=R} + K\left(\frac{\partial u}{\partial \rho}\right)_{\rho=R} = 0. \tag{12}$$

Set

$$\frac{H}{K} = h \tag{13}$$

and

$$\frac{m}{a^2} - p^2 = \lambda_m{}^2. \tag{14}$$

From (11), (12), (13) and (14) we obtain

$$\frac{Rh}{R\lambda_m} = \frac{J_1(R\lambda_m)}{J_0(R\lambda_m)}. \tag{15}$$

For the flat sides the procedure is similar and

$$\frac{bh}{bp} = tg(bp) \tag{16}$$

is obtained where $2b$ is the length of the cylinder. Both equations (15) and (16) have an infinite number of roots; each one determines a particular solution, which fulfills surface conditions.

From equations (11) and (14) the general solution will be:

$$u = \left[a_1 J_0(\rho\lambda_1)e^{-a^2\lambda_1{}^2t} + a_2 J_0(\rho\lambda_2)e^{-a^2\lambda_2{}^2t} + \cdots\right]\left[b_1\cos(p_1 z)e^{-a^2p_1{}^2t} + b_2\cos(p_2 z)e^{-a^2p_2{}^2t} + \cdots\right] \tag{17}$$

The constants a_m and b_m may be determined according to Fourier. Their values are

$$a_m = u_i \frac{\frac{1}{\lambda_m}J_1(R\lambda_m)}{\frac{R}{2}\left[1+\left(\frac{hR}{2\sqrt{\lambda_m}}\right)^2\right]J_0{}^2(R\lambda_m)}; \quad b_m = u_i \frac{2\sin(p_m R)}{P_m\left[R+\frac{1}{2}\frac{\sin(2p_m R)}{p_m}\right]} \tag{18}$$

where u_i is the initial temperature of the cylinder.

III. HYPOTHESIS NO. 3a.

Steam is formed at the boundary of the solid (Leidenfrost effect). The

water-steam surface remains parallel with the surface of the solid. Heat moves in the liquid by conduction alone.

In quantity production of hard steel articles such as balls and races for bearings, it was in some instances found that the outer surface of the quenched steel had soft spots which covered material of normal hardness. Structural investigation with the microscope indicated that a reheating of the surface, while quenching to a depth of a few tenths of a millimeter, had taken place.

In the following it is attempted to investigate mathematically the conditions under which a reheating of the surface occurs. It was suggested that at the instant of quenching the surface layer cools considerably. Immediately after this steam is formed which arrests any further cooling. The surface is then reheated by the hot central portion of the metal. In turn it will be shown that this view is not correct. At best, reheating may eventually occur in a later phase of the quenching, when local accumulation of steam has taken place.

Infinitely extended body with plain boundary.

In order to be able to treat the problem mathematically, it is necessary to choose the simplest conditions, *i.e.*, an infinite plainly bounded solid (Fig. 3). Furthermore, it will be assumed that the thickness of the steam layer formed is uniform; in other words, the boundary of the vapor and liquid remains parallel with the surface of the solid. This must be true as long as the steam layer is very thin. Assume that a bulging out would start at "*a*." Immediately. the poorly conducting layer would be increased in thickness, which in turn would reduce heat conduction at "*a*," counteracting further evaporation. In case of an approach "*b*" the opposite would happen. The evaporation would then tend to stabilize the surface of the liquid and would keep it of uniform thickness. With greater thickness the unevenness of the surface becomes relatively small, thus the stabilizing effect decreases, and the surface becomes unstable, and will break up into bubbles. The subsequent investigation should be regarded as an approximation and should be restricted to a short time interval, immediately after immersion. The main object is to decide whether or not a reheating may take place during this interval.

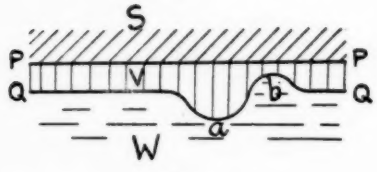

Fig. 3.

The phenomenon of soft surface occurs in water quenching of steel. We shall restrict our constants to steel, steam and water.

Notation.

Value of Constants Assumed in the Calculation.

K = coefficient of heat conductivity
- For steel we assume . . $K_1 = 0.1 \frac{\text{g cal.}}{\text{cm. sec. C.}^\circ}$;
- For superheated steam $K_2 \sim 10^{-4} \frac{\text{g cal.}}{\text{cm. sec. C.}^\circ}$ average v.;
- For water . . . . . $K_3 \sim 1.4 \times 10^{-3}$.

ρ = density . . . . .
- Steel . . . . . $\rho_1 = 7.8$ g/cm.^{3};
- Superheated steam . . . $\rho_2 = 3.10^{-4}$ g/cm.^{3} average;
- Water . . . . . $\rho_3 = 1.0$.

c = specific heat
- Steel . . . . . $C_1 = 0.114$;
- Superheated steam . . . $C_2 = 0.5$—average value;
- Water . . . . . $C_3 = 1.0$.

m = volume ratio steam/water = $\rho_3/\rho_2 = 3.33 \times 10^3$.

$a^2 = K/\rho C$ = diffusivity.

x = depth coördinate $x < 0$ within the steel.

$x = \xi$ boundary QQ (water, steam) at time t. (See Fig. 4.)

ξ' = thickness of layer of water which evaporated at time t.

λ = heat of evaporation (latent h). 540 cm. sec.

$\Theta(x) = 2/\sqrt{\pi} \int_0^x e^{-\beta^2} d\beta$ abbreviation for the probability integral.

u = temperature.

t = time.

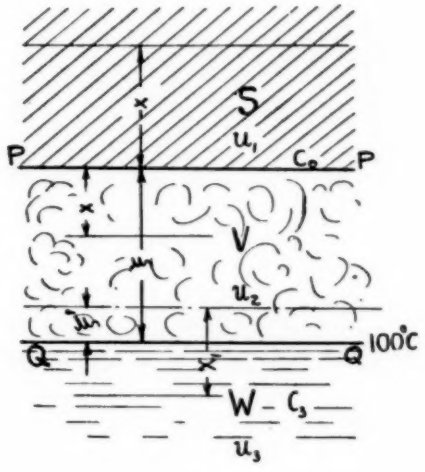

Fig. 4.

A, B, C, constants to be determined from the limiting conditions α, β are constants.

The differential equations governing the flow of heat are

$$\frac{\partial u_1}{\partial t} = a_1^2 \frac{\partial^2 u_1}{\partial x^2} \text{ in the steel,} \tag{19}$$

$$\frac{\partial u_2}{\partial t} = a_2^2 \frac{\partial^2 u_2}{\partial x^2} \text{ in the steam,} \tag{20}$$

$$\frac{\partial u_3}{\partial t} = a_3^2 \frac{\partial^2 u_3}{\partial x_1^2} \text{ in the water.} \tag{21}$$

At the plane QQ the heat of evaporation per second must equal the difference between gain and loss per second at the plane QQ, which gives the following equation:

$$K_2 \left(- \frac{\partial u_2}{\partial x} \right)_\xi = K_3 \left(- \frac{\partial u_3}{\partial x_1} \right)_{\xi'} + \lambda \rho_3 \frac{d\xi'}{dt} . \tag{22}$$

It may be verified by substitution, that the solutions of these differential equations are

$$u_1 = A_1 + B_1 \theta \left(- \frac{x}{2a_1 \sqrt{t}} \right); \tag{23}$$

$$u_2 = A_2 + B_2 \theta \left(\frac{x}{2a_2 \sqrt{t}} \right), \tag{24}$$

$$u_3 = A_3 + B_3 \theta \left(\frac{x_1}{2a_3 \sqrt{t}} \right) \tag{25}$$

$$\xi = \alpha \sqrt{t} \tag{26}$$

$$\xi' = \beta \sqrt{t} \tag{27}$$

$$\alpha = (m + 1)\beta. \tag{28}$$

The boundary conditions to be fulfilled are

$$x_1 = \xi', \qquad x = \xi, \qquad u_2 = u_3 = 100^\circ \text{ C.}$$

from (24), (25), (26), (27)

$$A_2 + B_2 \theta \left(\frac{\alpha}{2a_2} \right) = 100, \tag{29}$$

$$A_3 + B_3 \theta \left(\frac{\beta}{2a_3} \right) = 100. \tag{30}$$

for $x = 0$, $u_1 = A_1$; $u_2 = A_2$ denote

$$A_1 = A_2 \equiv C_0, \tag{31}$$

let the temperature of the water far away from the plate be $x_1 = \infty$, $u_3 \equiv C_3$, then

$$C_3 = A_3 + B_3 \tag{32}$$

from (29) and (31),

$$B_2 = \frac{100 - C_0}{\theta\left(\frac{\alpha}{2a_2}\right)} \tag{33}$$

from (30) and (32)

$$B_3 = \frac{C_3 - 100}{1 - \theta\left(\frac{\beta}{2a_3}\right)}. \tag{34}$$

We assume the initial temperature of the steel C_1, uniform at $t = 0$ and

$$u_1 \equiv C_1 \quad \text{for} \quad x = -\infty \tag{35}$$

from

$$C_1 = A_1 + B_1 \tag{36}$$

from

$$u_1 = C_0 + (C_1 - C_0)\theta\left(\frac{-x}{2a_1\sqrt{t}}\right). \tag{37}$$

In order to determine C_0 we have to remember that the gain and loss of heat at the boundary of the metal are equal, thus

$$K_1\left(-\frac{\partial u_1}{\partial x}\right)_{x=0} = K_2\left(-\frac{\partial u_2}{\partial x}\right)_{x=0} \tag{38}$$

if the values u_1 and u_2 from (23) and (24) be substituted

$$-\frac{K_1 B_1}{a_1} = \frac{K_2 B_2}{a_2}, \tag{39}$$

substituting the values for B_1 and B_2

$$C_0 = \frac{100 + C_1 \frac{K_1}{K_2}\frac{a_2}{a_1}\theta\left(\frac{\alpha}{2a_2}\right)}{1 + \frac{K_1}{K_2}\frac{a_2}{a_1}\theta\left(\frac{\alpha}{2a_2}\right)} \tag{40}$$

from (22) we obtain

$$C_0 = 100 + \left[\lambda\rho_3 \frac{\sqrt{\pi}}{2} \frac{a_2}{K_2} \theta\left(\frac{\alpha}{2a_2}\right) \beta e^{(1/2a_2)^2 a^2} + \frac{a_2 K_3}{a_3 K_2} \frac{100 - C_3}{1 - \theta\left(\frac{\beta}{2a_3}\right)} \theta\left(\frac{\alpha}{2a_2}\right) e^{(1/2a_2)^2 a^2 - (1/2\beta_3)^2 \beta^2} \right]. \tag{41}$$

(40) and (41) contain α and C_0 as the only unknown quantities.

Introducing the numerical values of the constants it is possible to determine by trial the values of α and C_0. For steel and water of the temperature of 0° C.

$$C_1 - C_0 = 12.6° \text{ C.}$$

and

$$\alpha = 0.0336 \text{ cm. sec.}^{-1/2}. \qquad \text{(See Fig. 9.)}$$

This means that the temperature at the surface of an infinite body of steel drops 12.6° C. when quenched in ice cold water and remains at that temperature. The temperature gradually drops to this value within the body as per equation (37).

It would be interesting to compare the heat per second lost by conduction with that used for evaporating the water.

$$\frac{Q_C}{Q_\lambda} = \frac{\frac{K_3}{a_3} \frac{C_3 - 100}{1 - 0} m}{\lambda\rho_3 0.886\alpha} = \frac{\frac{1.4 \times 10^{-3}}{0.0374} \times 100 \times 3.33 \times 10^3}{540 \times 1 \times 0.886 \times 0.0336} = 775.$$

From this we arrive to the conclusion that the latent heat is negligible compared with the conducted heat. This is explained by the great expansion of the water when converted to steam. *A very slight evaporation causes a comparatively great increase of thickness of the steam layer* thus decreasing the outflow of heat, while the heat conducted away is independent of the thickness of the steam layer. This holds good until the thickness of the steam layer becomes large enough to render it unstable and bubbles begin to form. Then the layer is broken down and new contact is formed, new evaporation sets in and the cooling will proceed at a higher rate than obtained by equation (37). Vigorous bubbling takes place also when quenching steel in hot water and by the evaporation at repeated contacts, it is possible to obtain hard quenching even in boiling water.

Plate of finite thickness, quenched on both sides.

In the preceding section it was shown that the surface temperature of a large piece of steel quenched in water will suddenly drop by an in-

significant amount, and remain at that temperature, provided the assumptions on which the solution of the problem is based are fulfilled. When quenching large masses of steel it may actually be noticed that the surface remains incandescent for a considerable length of time after submersion.

Furthermore, it is borne out that under these assumptions a *temperature rise after the first drop would not occur.*

It would be of further interest to extend the investigation to a plate of finite thickness quenched at both sides. Evidently the solution would be identical with the one of the preceding section until the temperature drop reached the center of the plate; after this the surface temperature must gradually drop below C_0.

1. The amount of heat absorbed by the water at QQ (Fig. 4) may be easily determined as QQ must be at the constant temperature of 100° C. The classical solution (convection excluded) is

$$u_3 = 100\left(1 - \theta\left[\frac{x_1}{2a_3\sqrt{t}}\right]\right). \tag{42}$$

The heat current thus is

$$K_3\left(\frac{\partial u_3}{\partial x_3}\right) = -100K_3\left[\frac{2}{2a_3\sqrt{\pi t}}e^{-(x_1/2a_3\sqrt{t})^2}\right]_{x_1=0} = -100K_3\frac{1}{a_3\sqrt{\pi t}}. \tag{43}$$

2. This same heat current must be emitted by PP (Fig. 4) as the capacity of the film, and the heat used in evaporating the liquid is negligible as long as the assumption of parallelism of QQ and PP is valid. Equation (43) thus furnishes one boundary condition. The second boundary condition is given by the symmetry. According to this, there is no heat exchanged through the center plane of the plate. This is expressed by

$$\left(\frac{\partial u_1}{\partial x}\right)_{x=0} = 0. \tag{44}$$

Besides the terminal conditions (43) and (44) the differential equation

$$\frac{\partial u_1}{\partial t} = a_1^2\frac{\partial^2 u_1}{\partial x^2}$$

must be fulfilled. This problem has also been solved under the premises defined at the beginning of this article. The details of the exact solution will not be given here as it would occupy considerable space. Only the final result is presented in Fig. 5. "c" is the temperature-time curve

at the surface of a plate 2 cm. thick, quenched in ice-water. Curve "b" refers to a depth 0.05 cm. below the surface. If, however, the temperature drops slowly, its distribution within the plate must be nearly uniform, which permits solving the problem in an approximate way.

Denote the initial temperature by u_i. Let the heat contained in a prism of 1 cm.^{2} section, extending from the center to the surface, be Q_i. The rate of change of Q_i must be equal to the heat lost per cm.^{2} surface per second, or

$$\frac{dQ}{dt} = K_3\left[\frac{\partial u_3}{\partial x}\right]_{x=0} = -100K_3\frac{1}{a_3\sqrt{\pi t}},$$

$$Q = -100\frac{K_3}{a_3}\frac{2}{\sqrt{\pi}}\sqrt{t} + Q_i,$$

$$Q = uc_1\rho_1 l \qquad Q_i = u_i c_1\rho_1 l.$$

The approximate solution thus is

$$u_i - u = 100\frac{K_3}{a_3 c_1\rho_1 l}\frac{2}{\sqrt{\pi}}\sqrt{t}$$

$$= 100\frac{1.4\times10^{-3}}{3.74\times10^{-2}\times0.114\times7.8\times1}\cdot\frac{2}{\sqrt{\pi}}\sqrt{t} = 4.76\sqrt{t}$$

for a plate 2 cm. thick (l = 1 cm.). For comparison this approximate solution is represented by the dotted line "a" (Fig. 5) which approaches very closely the accurate solution represented by C after a few seconds.

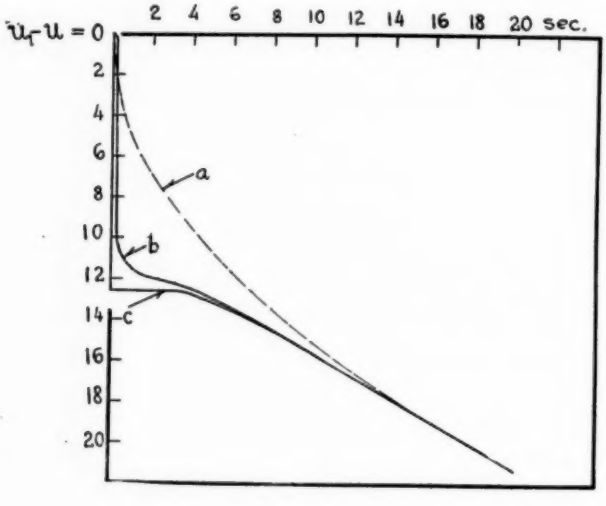

Fig. 5.

IV. HYPOTHESIS 3*b*.

Steam is formed at the boundary of the solid. The surface water-steam remains parallel to the surface of the solid. Heat is removed by convection only, at a uniform rate.

The boundary surface of water-steam QQ in Fig. 4 must be at 100° C. Consider the simplest case of uniform turbulence, in which case the rate of removal of heat is constant. Due to the fact that the heat capacity of the steam layer is negligible, the same amount of heat is removed from the metal surface as from the water-steam surface. The amount of heat required to evaporate the liquid must be negligible. (See Hypothesis No. 3*a*.)

Let us assume a plate quenched on both sides. It should be of uniform initial temperature. What will be the temperature at any point of the plate at any time after quenching, if the boundary conditions mentioned above are valid?

$$\frac{\partial u}{\partial t} = a^2 \frac{\partial^2 u}{\partial x^2}, \tag{45}$$

differentiating with respect to x,

$$\frac{\partial}{\partial t}\left(\frac{\partial u}{\partial x}\right) = a^2 \frac{\partial^2}{\partial x^2}\left(\frac{\partial u}{\partial x}\right), \tag{46}$$

denote

$$\frac{\partial u}{\partial x} = v, \tag{47}$$

$$\frac{\partial v}{\partial t} = a^2 \frac{\partial^2 v}{\partial x^2}, \tag{48}$$

boundary conditions

$$\text{(49)} \quad \text{at center} \left| -K\frac{\partial u}{\partial x}\right|_{x=0} = |-Kv|_{x=0} = 0,$$

$$\text{(50)} \quad \text{at surface} \left| -K\frac{\partial u}{\partial x}\right|_{x=l} = |-Kv|_{x=l} = C_2 H = \text{constant},$$

(51) $t = 0 \quad u = u_i$ constant within the plate.

Equation (48) has the form of equation (45). The corresponding solution with boundary conditions (49), (50) and (51) is generally known, and may be written

$$v = -\frac{2\pi a^2}{l^2} \sum_{m=1}^{\infty} (-1)^m m \sin\left(\frac{m\pi x}{l}\right) \int_0^t e^{-a^2(m\pi/l)^2(t-\tau)} \frac{C_2}{K} H d\tau, \tag{52}$$

where C_2 designates the temperature at QQ above the temperature of

the surrounding liquid. We shall assume ice-cold water, in which case $C_2 = 100°$ C.

$$(53) \qquad \int_0^t e^{-(am\pi/l)^2(t-\tau)}\, d\tau = \left(\frac{l}{amn}\right)^2 (1 - e^{-(am\pi/l)^2 t}).$$

For abbreviation let us set

$$(54) \qquad z = \left(\frac{a\pi}{l}\right)^2 t;$$

then

$$(55) \qquad v = \frac{2C_2H}{\pi K} \sum_{m=1}^{\infty} \frac{(-1)^m}{m} \sin\left(\frac{m\pi x}{l}\right)(1 - e^{-m^2 z}).$$

Let the difference of temperature between center and at the point x be Δu_x. From (47)

$$(56) \quad \Delta u_x = \int_0^x \frac{\partial v}{\partial x} dx = \frac{2lC_2H}{\pi^2 K_1} \sum \frac{(-1)^m}{m^2} \left(\cos\left(\frac{m\pi x}{l}\right) - 1\right)(1 - e^{-m^2 z}).$$

In order to be able to determine the drop of temperature at the center below its initial value, equate HC_2t (which is the heat lost through the surface), to the loss of heat in the plate.

$$(57) \qquad l\rho c(u_i - u_{x=0}) + c\rho \int_0^l \Delta u_x dx = HC_2 t.$$

Substituting the value of Δu_x from (56) in (57), and integrating, the temperature drop at any point of the plate may be expressed by

$$(58) \quad u_i - u_x = \frac{2}{\pi^2} l \frac{H}{K} C_2 \left[\sum_{m=1}^{\infty} \frac{(-1)^m}{m^2} \cos\left(\frac{m\pi x}{l}\right)(1 - e^{-m^2 z}) + \frac{z}{2}\right].$$

The steady state is represented by the linear equation

$$u_1 - u_x = A\frac{z}{2},$$

i.e., the temperature drop is proportional to the time, which is self-evident when considering the premises. Equation (58) is plotted on Fig. 6. The temperature time lines at different depths are parallel.

V. HYPOTHESIS NO. 4.

Effect of sudden stop of quenching.

Under No. 3*a* it has been pointed out that a thin soft shell is occasionally found on hard steel articles which were quenched in water. This phenomenon seems to be promoted by warm quenching water and when the quenched pieces touch each other at the bottom of the quenching tank.

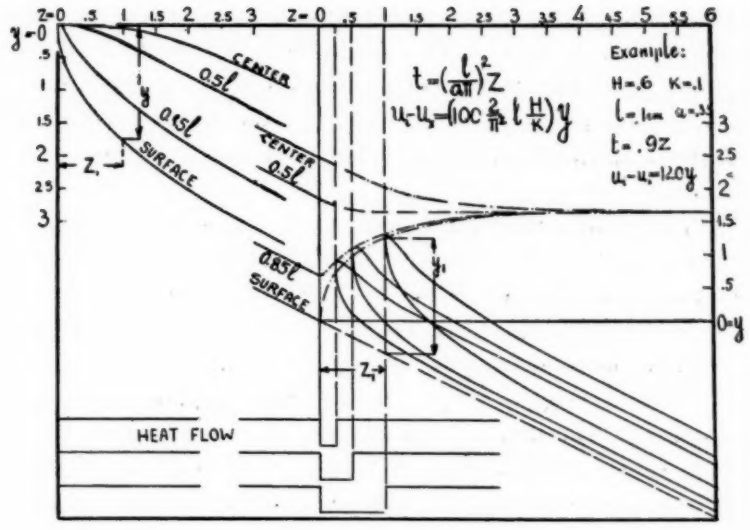

Fig. 6.

It was shown that reheating cannot occur immediately after quenching. All that happens then is a sudden but small drop of temperature to a value which remains constant at the surface untli either the temperature drop reached the center, or the film becomes too thick; the film then collapses and bubbling begins.

The only other explanation of surface reheating is a stop in the flow at a later phase of the cooling process.

According to Portevin, the transformation of structure to hard martensite begins around 300° C. Occasionally microscopic investigations of water-quenched specimens reveal "tempered" needles of martensite at the surface, which postulates the preëxistence of martensite, consequently a temperature of at least 300° C. must have been reached at the surface, after which the temperature must have been raised, so as to produce the tempering.

We shall not enter into speculation about the nature of the obstruction which causes a reheating of the surface, but postulate an ideal case, *i.e.*, an instantaneous and complete arrest of a constant flow of heat. This is a drastic condition but may serve as a point of departure for estimating milder cases.

Let us further suppose that after an arbitrary time limit the obstruction is instantaneously removed and original quenching condition reestablished.

The problem of interrupted heat flow may be solved in a simple way

when considering that the underlying differential equation is a linear one, with constant coefficients. This equation is satisfied by the sum of any number of particular solutions. The physical interpretation of this fact is the principle of superposition, *i.e.*, the coexistence of different flows without mutual disturbance. The resultant flow is the sum of the components.

This principle may be applied with advantage to the present problem. The solution may result from two heat currents in opposite direction, and the fictitious influx would set in at the time when the arrest of the influx in the original problem begins. According to the principle of superposition the two currents, equal and opposite, counteract each other, the result being a stop of flow. The graphical construction is thus as follows: The temperature-curve which corresponds to a *constant* outflux of heat at the surface is first plotted (Equation (58)). The moment of arrest of heat on the time scale is then marked, and regarded as a second origin. The drop in the first system (say y_1, in Fig. 6) at a given time (z_1), is added to the system defined by the second origin as indicated in Fig. 6.

Fig. 6 is drawn on a general scale, which may be specialized to given constants. This is shown in an example. $H = 0.6$ g. cal. cm.$^{-2}$ sec.$^{-1}$ C.$^{\circ -1}$ is assumed, which is the highest value computed in the following article. From Fig. 6 it is obvious that an increase in the intensity of quenching (H) increases the maximum temperature rise in reheating. At $0.85l$ (1.5 mm. depth on a 2 cm. plate) the maximum reheating would be considerably less (about 57 per cent. of the surface). The decrease of the relative maximum reheating does not depend on the quenching speed if the premises of our deductions are valid. An overheating at any point closer than 0.5 to the center is not possible under the assumed cooling law.

To be able to form an idea about the magnitude of reheating, let us assume an example.

For $H = 0.6$ g. cal. cm.$^{-2}$ sec.$^{-1}$ C.$^{\circ -1}$; $l = 1$ cm. (thickness of plate $= 2$ cm.);

$K = .1$ g. cal. cm.$^{-1}$ sec.$^{-1}$ C.$^{\circ -1}$; $a = 0.33$ cm. sec.$^{-1/2}$.

The increase of temperature after a stop lasting for 0.45 second, is 120° C. at the surface and 48° at a depth of 1.5 mm. In 0.9 second this would increase to 150° C. and 72° C. respectively. With an arrest of flow for an indefinite time, the temperature rise would be 200° C. at the surface.

VI. Discussion of the Results and Comparison with Test Data.

In the foregoing articles four cooling hypotheses were examined, each

one leading to a solution characteristic of the surface cooling. In every case it was assumed that the constants of the metal do not vary with the temperature and no heat was liberated within the metal during quenching. The results derived in the first two cases are exponential functions, *i.e.*, the steady state appears as a straight line if time is plotted to a uniform scale and the corresponding temperature to a logarithmic scale. In the third case the steady state is a parabolic curve, *i.e.*, straight on a double logarithmic paper. In the fourth case the relation between time and temperature is linear.

Experimental cooling curves by Portevin[2] on water quenching of cylinders are plotted on semi-logarithmic paper. Also curves for Ni Si cylinder by Pilling and Lynch[3] and for steel cylinder by Honda[4] are plotted for comparison. (Fig. 7.) The abscissa were shifted in some cases to avoid the starting condition, *i.e.*, before steady state was reached.

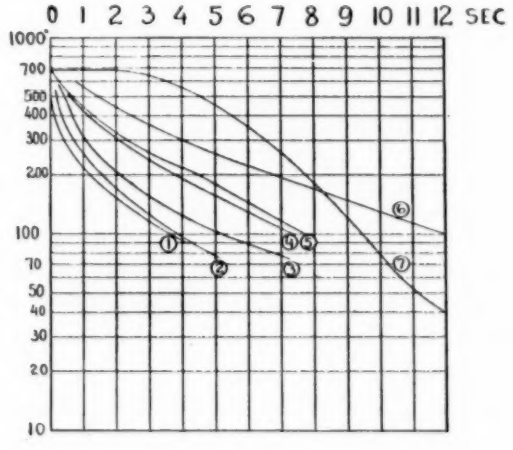

Fig. 7.

1. Silver cylinder 0.8 cm. dia. × 2.4 cm. long, quenched in running tap water, by Portevin and Garvin.

2. Silver cylinder 1.2 cm. dia. × 3.6 cm. long, quenched in running rap water, by P. and G.

3. Silver cylinder 2 cm. dia. × 6 cm. long, quenched in running tap water, by P. and G.

4. Nickel cylinder 1.2 cm. dia. × 3.6 cm. long, quenched in running tap water, by P. and G.

5. 95 per cent. Ni + 5 per cent. Si; cylinder 0.64 cm. dia. 5 cm. long, quenched in water or 1° C., by Pilling and Lynch.

6. Nickel cylinder 2 cm. dia. × 6 cm. long, quenched in running tap water, by Portevin and Garvin.

7. Steel cylinder 1.26 per cent. C, 2 cm. dia. × 2 cm. long, quenched in water, by Honda.

None of the curves are straight lines at high temperatures. The heavier pieces show an almost straight course at a later phase of cooling. This indicates that the surface soon reaches the constant temperature as per Article I. In other words, the larger the mass, or lower the con-

ductivity, the more accurately will the hypothesis of instantaneous surface cooling apply, when points in the vicinity of the center are considered.

The fact that at higher temperatures the experimental curves do not appear as straight lines, if plotted on semi-logarithmic paper, is a proof that Newton's cooling constant depends on the surface temperature. For a short interval it is legitimate to regard H constant, and it is possible to determine its approximate value from the curves obtained by experiment. The determination is the more accurate the smaller the difference of temperature between surface and center. In this case the conception of steady flow may be maintained, which would be expressed by the fact that the temperature-time-space equation may be reduced to the first member of the series.

For the cylinder (Equation 17)

$$u = a_1 b_1 J_0(\rho\lambda_1) \cos(z\rho_1) e^{-a^2(\lambda_1^2+p_1^2)t}. \tag{59}$$

$$\text{Set } a^2(\lambda_1^2 + p_1^2) = m. \tag{60}$$

Take the logarithm of both members of the equation (59)

$$\log_{10} u = \log_{10}(a_1 b_1 J_0(\rho\lambda_1) \cos(zp_1)) - mt \log_{10} e.$$

This equation appears as a straight line on semi-logarithmic paper, $-mt$ being the slope of the line. By drawing tangents to the experimental cooling curve, it is possible to determine the instantaneous values of m. Thus equations (15), (16) and (60) contain three unknown quantities λ_1, p_1 and h, which may be determined. $H = Kh$ by definition.

The surface temperature which corresponds to the instantaneous value of H, at a given center temperature, may be determined from equation

$$\frac{u_s}{u_c} = \frac{J_0(R\lambda_1)}{J_0(0)} = J_0(R\lambda_1). \tag{59}$$

The value of H has been derived from three of the experimental curves shown in Fig. 7.

Curves No. 1 and No. 3 refer to 0.8 cm. dia. $\times$ 2.4 cm. long and 2 cm. $\times$ 6 cm. silver cylinders respectively. Curve No. 5 shows cooling of a 0.64 $\times$ 5 cm. cylinder consisting of 95 per cent. N; and 5 per cent. Si. The good heat conductivity of the former and the small diameter of the latter specimen may justify the assumption of "steady flow," when determining H. The greatest temperature drops between center and surface are: 8 per cent., 24 per cent., and 10 per cent. respectively.

In Fig. 8 values of H are plotted against the surface temperature on semi-logarithmic paper. From this it appears that at higher temperatures H is an exponential function of the temperature, thus it is far from being constant. This is also borne out by a preliminary experiment made on electrically heated wire submerged in petroleum.

The absolute size of the specimen also seems to have an influence on the magnitude of H. The smaller the specimen, the smaller H seems to be.

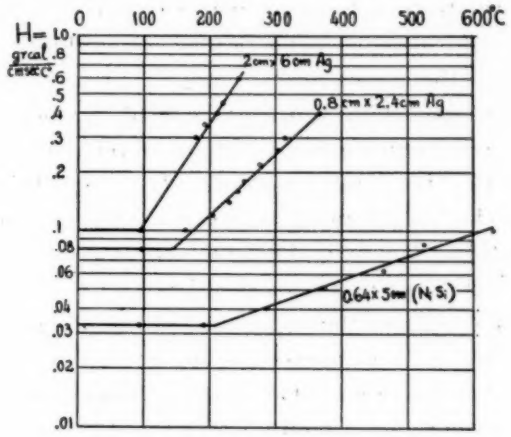

Fig. 8.

Comparison of the experimental curves with solutions obtained in Article 3*a* and 3*b* bears out the fact that Hypothesis 3*a* is untenable after the first stage of quenching. It results in a too slow cooling as compared with experiment. The fact that the experimental curves are not straight lines as shown in the articles by Portevin, Honda and Pilling, is a proof that neither is Hypothesis 3*b* valid. This may be explained by the fact that the thickness of the steam film grows rapidly (Fig. 9),

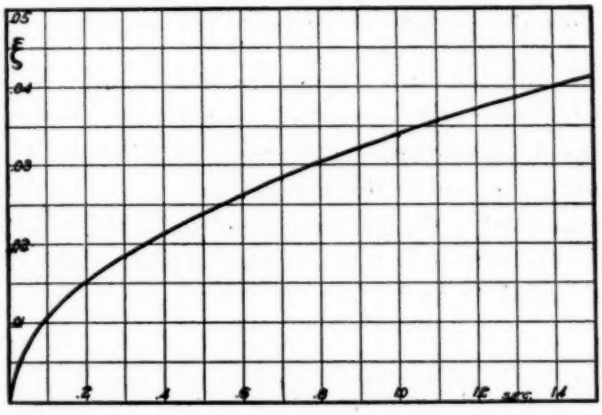

Fig. 9.

becomes unstable and bubbling sets in, which renders a mathematical treatment difficult. That bubbling sets in is also indicated by the vibration, which is transmitted by the liquid to the surface of the tank, where it may be felt.

CONCLUSIONS.

1. It has been shown that it is possible to calculate the temperature in the vicinity of the center but not at the surface of a regularly shaped body, provided the body is large, or it is a poor conductor of heat. In such cases the substitution of water in place of oil does not improve the quenching speed at the center.

2. An increase of quenching temperature results in increased quenching speed at a given lower temperature. This is important in the practice of hardening of steel. It is impossible to obtain good hardness if the specimen is quenched at a temperature just above the critical.

3. Newton's cooling law may also be interpreted as a constant surface resistance (scale) obstructing emission of heat.

4. A very rapid cooling of the surface to low temperatures in quenching media similar to water, with immediate reheating due to formation of a steam jacket, is not possible. The surface temperature drops instantaneously by an insignificant amount, which is followed by a gradual drop.

5. Assuming a constant rate of heat emission, which is suddenly stopped, a reheating of the surface is possible. The amount of reheating is the greater the swifter the drop preceding the arrest of flow. Reheating cannot occur at the vicinity of the center.

6. The specific surface emission is not proportional to the surface temperature, but Newton's "constant" increases exponentially with the temperature. It seems also to depend on the absolute size of the quenched object, smaller sizes having smaller specific emission. This would point to a difficulty in obtaining very great quenching speeds by trying to reduce the diameter of the quenched specimen.

In conclusion, I wish to acknowledge my appreciation to S K F Research Laboratory and particularly to Dr. Styri, for originally suggesting this work, and to S K F Industries, Inc., New York, for granting the opportunity to complete this investigation.

I am also indebted to the following members of the S K F Laboratory for their valuable assistance in preparing this paper: Messrs. H. Sjövall, W. F. Titus, and H. O. Walp.

THE STRESS-ENERGY TENSOR IN ELECTROMAGNETIC THEORY AND A NEW LAW OF FORCE.

BY H. BATEMAN.

SYNOPSIS.

Modified Electromagnetic Theory.—By suitably modifying the equations for the components of the stress-energy tensor it is possible to reconcile electromagnetic theory with the idea of non-radiating electronic orbits. The change, however, is equivalent to assuming that an element of electricity is acted upon by a *new force* which depends on the gradient of the density of electricity and balances the usual electromagnetic force. By assuming a certain *distribution of density within an electron* it is also possible to account for the existence of discrete electronic charges.

1. *The Stress-energy Tensor.*—We shall assume that the stress-energy tensor associated with a system of electric charges has the following components:

$$W = \tfrac{1}{2}(E^2 + H^2) + \frac{2}{c^2}\psi\frac{\partial^2\psi}{\partial t^2} + \left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 - \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2;$$

$$S_x = c[E_yH_z - E_zH_y] - 2\psi\frac{\partial^2\psi}{\partial x\partial t}, \qquad \text{etc.};$$

$$X_x = \tfrac{1}{2}[E_x^2 - E_y^2 - E_z^2 + H_x^2 - H_y^2 - H_z^2] - 2\psi\frac{\partial^2\psi}{\partial x^2} + \left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 - \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2;$$

. . . . . .

$$Y_x = X_y = E_xE_y + H_xH_y - 2\psi\frac{\partial^2\psi}{\partial x\partial y}, \qquad \text{etc.}$$

The quantity W represents the density of energy, the vector S specifies the flow of energy and is proportional to the density of momentum; the six quantities X_x, Y_y, Z_z, Y_z, Z_x, X_y are the components of stress; v is the velocity of electricity at a point (ξ, η, ζ) where the density of electricity at time τ is ρ; E and H are the field vectors in the electromagnetic field produced by the electric charges and ψ is a retarded potential defined by the equations

$$\psi = \frac{1}{4\pi}\int\frac{d\xi d\eta d\zeta}{r}\left[\rho\sqrt{1 - \frac{v^2}{c^2}}\right],$$

$$r^2 = (x - \xi)^2 + (y - \eta)^2 + (z - \zeta)^2 = c^2(t - \tau)^2, \qquad \tau < t,$$

c being the velocity of light.

The components of the total force F are given by the three equations of type

$$F_x = \frac{\partial X_x}{\partial x} + \frac{\partial Y_x}{\partial y} + \frac{\partial Z_x}{\partial z} - \frac{1}{c^2}\frac{\partial S_x}{\partial t}$$

and we find that

$$F_x = \rho\left[E_x + \frac{1}{c}(v_y H_z - v_z H_y)\right] - 2\psi\frac{\partial}{\partial x}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}\right]$$

$$= \rho\left[E_x + \frac{1}{c}(v_y H_z - v_z H_y)\right] + 2\psi\frac{\partial}{\partial x}\left[\rho\sqrt{1 - \frac{v^2}{c^2}}\right].$$

The energy equation

$$\frac{\partial S_x}{\partial x} + \frac{\partial S_y}{\partial y} + \frac{\partial S_z}{\partial z} + \frac{\partial W}{\partial t} = -(v \cdot F)$$

requires that

$$\psi\frac{d}{dt}\left[\rho\sqrt{1 - \frac{v^2}{c^2}}\right] = 0,$$

where

$$\frac{d}{dt} = \frac{\partial}{\partial t} + v_x\frac{\partial}{\partial x} + v_y\frac{\partial}{\partial y} + v_z\frac{\partial}{\partial z}.$$

It seems reasonable to adopt the hypothesis that F is everywhere zero.

2. *The Existence of Discrete Charges.*—When all the electric charges are stationary ψ becomes the electrostatic potential and

$$F_x = -\rho\frac{\partial\psi}{\partial x} + 2\psi\frac{\partial\rho}{\partial x}.$$

consequently F vanishes everywhere if

$$\rho\frac{\partial\psi}{\partial x} = 2\psi\frac{\partial\rho}{\partial x},$$

$$\rho\frac{\partial\psi}{\partial y} = 2\psi\frac{\partial\rho}{\partial y},$$

$$\rho\frac{\partial\psi}{\partial z} = 2\psi\frac{\partial\rho}{\partial z},$$

and this means that

$$\psi = b^2\rho^2,$$

where b^2 is a constant. The function ψ then satisfies the partial differential equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{1}{b}\sqrt{\psi} = 0.$$

Let us consider the case in which ρ is a function of the radius r from a point o and differs from zero only within a sphere of radius a. Assuming that

$$\rho = A_0 + A_2\left(\frac{r}{a}\right)^2 + A_4\left(\frac{r}{a}\right)^4 + \cdots,$$

we find that

$$\psi = \frac{1}{3\cdot 2}(3a^2 - r^2)A_0 + \frac{1}{4\cdot 5}\left(5a^2 - \frac{r^4}{a^2}\right)A_2 + \frac{1}{6\cdot 7}\left(7a^2 - \frac{r^6}{a^4}\right)A_4 + \cdots;$$

consequently

$$b^2\left[A_0 + A_2\left(\frac{r}{a}\right)^2 + A_4\left(\frac{r}{a}\right)^4 + \cdots\right]^2 = \frac{1}{2\cdot 3}(3a^2 - r^2)A_0 + \frac{1}{4\cdot 5}\left(5a^2 - \frac{r^4}{a^2}\right)A_2 + \cdots.$$

Equating coefficients we find that

$$\rho = A_0\left[1 - \frac{1}{12}\frac{r^2}{A_0 b^2} - \frac{1}{720}\frac{r^4}{A_0^2 b^4} - \frac{1}{10080}\frac{r^6}{A_0^3 b^6} - \frac{31}{6!\,7!}\frac{r^8}{A_0^4 b^8} - \frac{(971)(24)}{(6!)(11!)}\frac{r^{10}}{A_0^5 b^{10}} - \cdots\right],$$

$$f(\xi) \equiv 1 - \frac{1}{2}\xi + \frac{1}{48}\xi^2 + \frac{1}{4320}\xi^3 + \frac{1}{80640}\xi^4 + \frac{31}{(10)(6!)(7!)}\xi^5 + \frac{(971)(24)}{(6!)(12!)}\xi^6 + \cdots.$$

The equation $f(\xi) = 0$ has two roots, one of which is approximately $2\cdot 2$; the second is difficult to determine accurately as it is necessary to consider a large number of terms of the series; it appears to lie between 12 and 6 and is probably about 11.

When a and the total charge e are given, A_0 and b are determined, but there are two possible solutions and so there are two different types of discrete charge.[1] The present analysis does not, however, indicate the size of the electron.

[1] It is interesting to compare the solution of the equation $\psi = b^2\rho^2$ with that of the simpler equation $\psi = b^2\rho$ which would also lead to discrete charges. In the latter case we may have

$$\psi = \frac{1}{r}\sin\left(\frac{r}{b}\right) = b^2\rho,$$

the radius of the sphere being determined by the equation $a = b\pi(n + \frac{1}{2})$, where n is an integer. We have in fact

$$\psi = \int_r^a \rho r\,dr + \frac{1}{r}\int_0^r \rho r^2 dr = \frac{1}{b^2}\int_r^a \sin\left(\frac{r}{b}\right)dr + \frac{1}{b^2 r}\int_0^r \sin\left(\frac{r}{b}\right)r\,dr = \frac{1}{r}\sin\left(\frac{r}{b}\right).$$

The total electric charge is then

$$e = \int_0^a \rho r^2 dr = \sin(n + \tfrac{1}{2})\pi = (-1)^n$$

3 *The Radiation of Energy from a Moving Electric Pole.*—In the case of a moving point charge of electricity we must put

$$\psi = -\frac{e}{4\pi M}\sqrt{c^2-\xi'^2-\eta'^2-\zeta'^2} = -\frac{e}{4\pi M}\sqrt{c^2-v^2},$$

where $\xi(\tau)$, $\eta(\tau)$, $\zeta(\tau)$ are the coördinates of the charge e at time τ and M is defined as a function of x, y, z, t by the equations

$$M = [x-\xi(\tau)]\xi'(\tau) + [y-\eta(\tau)]\eta'(\tau) + [z-\zeta(\tau)]\zeta'(\tau) - c^2(t-\tau)$$
$$[x-\xi(\tau)]^2 + [y-\eta(\tau)]^2 + [z-\zeta(\tau)]^2 = c^2(t-\tau)^2$$
$$\tau < t.$$

Calculating S_x and retaining only terms of order $1/M^2$ we have

$$S_x \sim \frac{e^2c^2(t-\tau)(x-\xi)}{16\pi^2M^4}\left[\left\{v'^2 - 2(vv')\frac{K}{M} - (c^2-v^2)\frac{K^2}{M^2}\right\}\right.$$
$$\left. + 6(vv')\frac{K}{M} + 6(c^2-v^2)\frac{K^2}{M^2} - 2v'^2 - \frac{2(vv')^2}{c^2-v^2} - 2(vv'') - \frac{2L}{M}(c^2-v^2)\right],$$

where

$$K = (x-\xi)\xi'' + (y-\eta)\eta'' + (z-\zeta)\zeta'',$$
$$L = (x-\xi)\xi''' + (y-\eta)\eta''' + (z-\zeta)\zeta'''.$$

To calculate the radiation we must first of all replace $(x-\xi)$ in S_x by $c(t-\tau)$ to get the radial component of S. We must next multiply by a Doppler factor and this[1] is equivalent to replacing $(x-\xi)$ in S_x by $-M/c$. The final step is to integrate over a large sphere whose center is at the pole. Writing

$$I_n^m = \int_0^\pi \frac{\cos^m\theta \sin\theta d\theta}{(c-v\cos\theta)^n}$$

we have

$$I_3^0 = \frac{2c}{(c^2-v^2)^2}, \qquad I_4^1 = \frac{8cv}{3(c^2-v^2)^3},$$

$$I_5^0 = \frac{2c(c^2+v^2)}{(c^2-v^2)^4}, \qquad I_5^2 = \frac{2c(c^2+5v^2)}{3(c^2-v^2)^4},$$

and there is a different type of discrete charge for each positive integral value of n. In this case ρ is determined by a homogeneous linear integral equation while in the other case the integral equation is not linear. The equation $\psi = b^2\rho$ is used by A. Korn in his mechanical theory of the electromagnetic field. Phys. Zeitschr., Bd. 19 (1918), p. 234. Another distribution of density is considered by G. Mie, Ann. d. Phys., Bd. 39 (1912), p. 1.

[1] Cf. M. Abraham, Theorie der Elektrizität, Bd. II., p. 108. A Liénard, L'éclairage électrique (1898).

and we find that the rate of radiation is

$$R = \frac{e^2}{6\pi c^3}\left[\frac{\dot{v}^2 + (v\ddot{v})}{(c^2 - v^2)^2} + \frac{4(v\dot{v})^2}{(c^2 - v^2)^3}\right]$$

$$= \frac{e^2}{6\pi c^3}\frac{d}{d\tau}\left[\frac{(v\dot{v})}{(c^2 - v^2)^2}\right] = \frac{e^2}{12\pi c^3}\frac{d^2}{d\tau^2}\left[\frac{1}{c^2 - v^2}\right].$$

In a periodic motion the integral

$$\int R d\tau$$

taken over a complete period is zero and so there is no radiation of energy to infinity on the average.

It may be remarked that there is no radiation of energy to infinity when the components of the stress-energy tensor are given by[1]

$$W = \left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 + \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2 - \frac{1}{2}(E^2 + H^2),$$

$$S_x = -2\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial x} - c(E_yH_z - E_zH_y),$$

$$X_x = -\left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 + \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2$$

$$- \frac{1}{2}(E_x^2 - E_y^2 - E_z^2) - \frac{1}{2}(H_x^2 - H_y^2 - H_z^2),$$

$$X_y = Y_x = -2\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial y} - E_xE_y - H_xH_y,$$

but in this case the force is

$$F_x = 2\rho\sqrt{1 - \frac{v^2}{c^2}}\frac{\partial\psi}{\partial x} - \rho\left[E_x + \frac{1}{c}(v_yH_z - v_zH_y)\right]$$

and cannot be made to vanish at each point.

The present analysis does not lead to quantum theory because the electron has been treated as a point charge. It looks as if certain conditions may have to be satisfied in order that F may vanish everywhere when an electron of finite size describes an orbit round a positive nucleus. A discussion of this problem with the aid of the equations of § 1 looks difficult and will not be attempted here.

CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA,
April 10, 1922.

[1] The expressions depending on ψ are similar to those used by Volterra, Abraham and McLaren in the theory of gravitation. V. Volterra, Il Nuovo Cimento (1899), p. 337; M. Abraham, Phys Zeitschr. (1912), p. 1; S. B. McLaren, Phil. Mag., Oct., 1913, p. 635.

NOTE, ADDED JUNE 9, 1922.

It may be shown also that, when a point charge of electricity moves with an arbitrary velocity less than c, the rate at which linear momentum is radiated to infinity is the time derivative of a uniform function of the velocity and acceleration of the point charge. There is no radiation of momentum in a certain interval of time if the velocity and acceleration have the same values at the beginning and end of the interval.

With the new stress-energy tensor there appears also to be no radiation to infinity of angular momentum in the field of a Hertzian dipole.

Negative values of W may be avoided by introducing an additional stress-energy tensor corresponding to a universal constant negative pressure.

THE VARIATION OF THE INDEX OF REFRACTION OF WATER, ETHYL ALCOHOL, AND CARBON BISULPHIDE, WITH THE TEMPERATURE.

BY ELMER E. HALL AND ARTHUR R. PAYNE.

SYNOPSIS.

Index of Refraction of Pure Water for Sodium Light from 15° to 100° C.—Very few observations had previously been made for temperatures above 50° C. A precision spectrometer was used. The brass prism with optical glass windows was gold plated inside to prevent contamination of the pure gas-free water tested, and means were provided for keeping the temperature within 0.1° C. Many readings were taken and the average values are probably accurate to within about 0.00002. When reduced to vacuum they are well represented by the empirical formula: $n = 1.33401 - 10^{-7}(66t + 26.2t^2 - 0.1817t^3 + 0.000755t^4)$. The *temperature coefficient* dn/dt changes from $-8(10)^{-5}$ at 15° to $-30(10)^{-5}$ at 100°.

Index of Refraction of Commercially Pure Ethyl Alcohol and Carbon Bisulphide for Sodium Light from 15° up to the Boiling Points.—While Kahlbaum's ethyl alcohol, 99.8 per cent. absolute, and Baker's C.P. CS_2 were used, the absolute values obtained differ somewhat from those given by others for pure samples. Nevertheless the *temperature coefficients* are probably not affected by the slight amount of impurity present and are of interest because very few results are available for liquids at temperatures above 40° C. The results correspond to the empirical equations: dn/dt(ethyl alcohol, 15 to 70°) $= -10^{-6}[404 + 0.44(t - 15) + 0.0075(t - 15)^2]$; $dn/dt(CS_2$, 15 to 45°$) = -10^{-6}[766 + 5.12(t - 15) - 0.105(t - 15)^2]$.

Introduction.—Historically the study of the change in the index of refraction of liquids with change in temperature dates from the work of Jamin in 1856.[1] Most of the investigations made have been at temperatures not differing greatly from room temperature. In the case of water all the investigations, with two exceptions, are within the temperature range of 0° to 50° C. The two exceptions mentioned are the work of Ruhlman[2] and Kettler,[3] whose investigations included temperatures in the range 50 to 100° C. A partial bibliography for the three liquids mentioned in the title may be found in Landolt-Bornstein Tabellen. A brief incomplete historical summary for the case of water is given by Osborn.[4] Osborn's work is concerned only with the change in the index of refraction of water with the temperature, the absolute value of the index not being determined. For the range 1° to 38° C. he determined this change to approximately one unit in the seventh decimal place.

[1] Comptes Rendus, 43, 1191, 1856.

[2] Pogg. Ann., 132, 177, 1867.

[3] Ann. d. Phys., 33, 353 and 506, 1888.

[4] PHYS. REV., 2d series, 1, 198, 1913.

This work, together with the value of the index as found in such investigations as those of Walter,[1] Gifford[2] and Baxter, Burgess, and Daudt,[3] constitutes a very complete study for the range below 40° C. The data for the range above 40° seem to be somewhat uncertain, the work of Ruhlman and Kettler not being always in good agreement. It therefore seemed justifiable to the writers to study anew the index of refraction of water, especially in the region between 40° and 100° but making a sufficient number of determinations below 40° to enable a comparison to be made with other recent determinations. Determinations of the index of refraction of ethyl alcohol and carbon bisulphide from 15° C. to their boiling points are also included.

Apparatus and Method.—After preliminary trials of different methods, the spectrometer method was adopted. There was available a new precision spectrometer, designed by one of the writers, and built in the shop of the department of physics. The weight of the heavy telescope, counterpoise, and table was supported in part by ball bearings, the design thus permitting of a fairly heavy load on the spectrometer table. The instrument was provided with all needed slow motions, clamping devices and adjustments. The ten-inch circle, divided into one twelfth degrees, was cut on the automatic circular dividing engine which was also built in the shop of the department of physics.[4] By the use of two microscopes with travelling eyepieces, 180° apart, the scale could be read to one half seconds if desired. The circle was cut soon after the calibration of the dividing engine, and the engine and circle showed errors not exceeding eight seconds. It was found that errors of setting were slightly greater than errors of graduation. With the first prism described below readings were made for each temperature on different parts of the scale, attempting thereby to eliminate errors of graduation by using different parts of the scale. Errors in setting were cared for by taking the mean of a large number of settings. With the second prism described below a calibrated part of the scale was used.

Two different prisms and heating devices were used. In the first of these, used for water only, the prism had a refracting angle of approximately 75°. It was constructed of heavy brass, with optical glass plates clamped on the sides. These plates were carefully tested. The faces of the brass prism were first milled as true as possible and then ground down and polished with abrasive powder and rouge. The glass plates were placed directly against the polished brass. The cubical

[1] Ann. d. Phys., 46, 423, 1892.
[2] Roy. Soc. Proc., 78, 406, 1906.
[3] Am. Chem. Soc. Jr., 33, 1, 893, 1911.
[4] PHYS. REV., XXX., 492, 1910.

contents of the prism were 70 c.c. The water was kept well stirred by an electrically driven stirrer. The stirrer and the interior of the brass prism were heavily gold plated. It was found that enough brass would dissolve in the water in the course of a few hours to change the index of refraction by approximately two units in the fourth decimal place. The prism was placed inside a double-walled, jacketed and well-insulated, electrical heating device. This jacketed heater, which measured 17 cm. in diameter by 12 cm. high, was placed on the spectrometer table from which it was well insulated. The jacket was provided with sliding shutters over the windows of the prism, these shutters being kept closed except when a reading was being made. It was found that the temperature could be brought readily to any desired point and held there ndefinitely to within one tenth of a degree. The temperature was measured with a calibrated Baudin mercury thermometer placed close to the line of vision. As a check, and also to determine the uniformity of the temperature distribution within the water, two thermocouples were inserted, the galvanometer used being sensitive enough to detect changes of 0.1°.

In the second form of apparatus the prism, again of brass, gold plated, with optical glass sides, had an angle of approximately 60° and was surrounded, except over the windows, by an oil-bath heater. The oil was heated electrically in a forty-gallon tank and by a rotary pump made to circulate vigorously about the prism. The heaters within the tank were operated by a thermostat and the temperature control rendered automatic. The main advantage in this form of heater was in the time saved through the automatic control. The temperature remained constant to within one twentieth of a degree during the time of making a set of readings at any temperature. In this case the thermometer was nearly totally immersed, thus obviating the necessity of stem corrections. The cubical contents of this prism were about 1500 c.c. The prism angle was of course redetermined for each prism every time the prism was cleaned, and the value checked to be sure that it did not change with change in temperature during a set of measurements.

Purity of the Water.—Since very small amounts of impurities were found materially to change the index of refraction special care was taken to obtain chemically pure water. This was furnished by the chemistry department and was redistilled in block tin and condensed directly into "Resistenz" bottles. In this way it was kept practically free from gases and no impurities could be detected. The conductivity was not taken. The usual method of heating to the boiling point was used to keep the liquid gas-free during a set of readings. After gold plating the interior

of the prism contamination during use was practically eliminated. At a given temperature the water was often poured out, the prism washed and refilled and brought to the temperature under investigation with no change in the results.

Accuracy.—The index was calculated from the common minimum deviation formula. In determining the angle of minimum deviation the double angle was usually measured, that is, the prism was reversed and readings to the right and left of the zero setting taken. Six or seven readings were taken for each setting and with the first type of prism used these were repeated for different parts of the scale with the water held at a particular temperature. Readings taken throughout the temperature range were repeated during a period of several months and hence the values given represent the mean of a large number of readings. In determining the angle of the prism and the angle of minimum deviation the individual readings rarely differed from the mean by more than ten seconds and in most cases by much less than this amount. An error of ten seconds in the angle of minimum deviation introduced an error of approximately 3 units in the fifth decimal place with the 75° prism and 4 units in the fifth place with the 60° prism. An error of ten seconds in determining the angle of the prism introduced an error of approximately 2 units in the fifth place. It is believed that the final values for water relative to air given in Table II. are correct to within 2 units in the fifth place throughout the lower temperature range and to within 3 units in the fifth place for the higher temperature range. In Table IV. the values are reduced to the absolute index of refraction in order to compare them with the results of Kettler. In reducing the values observed in air to absolute values the question of distribution of the temperature gradient in the air outside the prism enters. Baxter, Burgess, and Daudt,[1] and others, have multiplied the value obtained in air by the index of refraction of air at the temperature of the water. Where the prism method is used this virtually assumes that the surfaces of equal temperature in the air outside the prism are normal to the direction of the incident and the emergent light. It is believed by the writers that with the prism used by them the more reasonable assumption is that the surfaces of equal temperature outside the prism are parallel to the faces of the prism, in which case it is the index of refraction of the air at room temperature which enters, irrespective of the temperature of the water in the prism. Hence in reducing the values to the absolute index the value obtained in air was, in each case, multiplied by 1.000272, the index of refraction of air at 20° C., which was approximately the room temperature throughout

[1] Loc. cit.

the investigation. At the highest temperature used the difference in the absolute index obtained by using the index of air at the room temperature and by using the index of air at the temperature of the water amounts to 8 units in the fifth place. Close to the prism faces the assumption made by the writers is doubtless nearest the truth; as one recedes from the prism faces, especially beyond the insulating jacket, the first assumption named more nearly represents the truth. The correct value therefore lies somewhere between the two. Of the two assumptions, if the one made by the writers be given the greater weight, then the error introduced by the uncertainty of the distribution of the temperature gradient in the air outside the prism cannot exceed 4 units in the fifth place at the highest temperature used. Hence the values of the index of refraction of water relative to vacuum are believed to be correct to within 2 units in the fifth place at approximately room temperatures, the possible error increasing with rise of temperature to perhaps three times this value at 100°. Changes in the index of refraction of air due to barometric changes affected the results by less than one unit in the fifth decimal place and were disregarded.

Results for Water.—In computing the observations for water where the actual temperatures differed by only a few tenths of a degree from integral values, the results were reduced to those for integral temperatures by interpolation. With this modification Table I. gives the experimental values obtained for the index of refraction of pure water relative to air for sodium light.

TABLE I.

The Index of Refraction of Pure, Gas-free Water, Relative to Air, for Sodium Light.

Temperature.	Index.	Temperature.	Index.	Temperature.	Index.	Temperature.	Index.
16° C.	1.33333	30° C.	1.33190	60° C.	1.32716	85° C.	1.32172
17	1.33325	40	1.33049	62	1.32678	87	1.32123
18	1.33317	44	1.32992	65	1.32616	90	1.32042
19	1.33308	48	1.32928	70	1.32510	93	1.31973
20	1.33298	50	1.32894	73	1.32444	95	1.31922
22	1.33284	52	1.32858	77	1.32354	97	1.31878
24	1.33262	55	1.32807	80	1.32284	98.4	1.31828
26	1.33241	56	1.32799	81	1.32259		
28	1.33220	58	1.32758	82.5	1.32218		

A large scale plot was made of the above values from which the values given in Tables II. and III. are taken.

In Tables III. and IV. the writers' values are compared with those of other observers. Table IV. is obtained from Table II. by multiplying

TABLE II.

The Index of Refraction of Pure Water, Relative to Air, for Sodium Light, obtained by Plotting the Results Given in Table I.

Temperature.	Index.	Temperature.	Index.	Temperature.	Index.	Temperature.	Index.
15° C.	1.33341	38° C.	1.33079	62° C.	1.32678	86° C.	1.32148
16.	1.33333	40.	1.33051	64.	1.32636	88.	1.32100
18.	1.33317	42.	1.33023	66.	1.32596	90.	1.32050
20.	1.33299	44.	1.32992	68.	1.32555	92.	1.32000
22.	1.33281	46.	1.32959	70.	1.32511	94.	1.31949
24.	1.33262	48.	1.32927	72.	1.32466	96.	1.31897
26.	1.33241	50.	1.32894	74.	1.32421	98.	1.31842
28.	1.33219	52.	1.32860	76.	1.32376	99.	1.31813
30.	1.33192	54.	1.32827	78.	1.32332	100.	1.31783
32.	1.33164	56.	1.32792	80.	1.32287		
34.	1.33136	58.	1.32755	82.	1.32241		
36.	1.33107	60.	1.32718	84.	1.32195		

by 1.000272, the refractive index of air. A column giving the variation of the index of refraction with the temperature is included in Table IV.

TABLE III.

Index of Refraction of Water, Relative to Air, Sodium Light.

Temperature.	Hall-Payne.	Walter.	Baxter-Burgess-Daudt.	Gifford.
15° C.	1.33341	1.33339		1.33343
16.	1.33333	1.33331		
18.	1.33316	1.33316		
20.	1.33299	1.33299	1.33299	
22.	1.33281	1.33281		
24.	1.33262	1.33261		
25.	1.33251	1.33251	1.33248	
26.	1.33241	1.33240		
28.	1.33219	1.33218		
30.	1.33192	1.33194	1.33190	

TABLE IV.

Absolute Index of Refraction of Water, Sodium Light.

Temp.	Kettler.	Hall-Payne.	dn/dt.	Temp.	Kettler.	Hall-Payne.	dn/dt.
15° C.	1.33365	1.33377	−0.00008	60° C.	1.32753	1.32754	− .00019
20.	1.33327	1.33335	− .00009	65.	1.32655	1.32652	− .00020
25.	1.33281	1.33287	− .00011	70.	1.32551	1.32547	−0.00021
30.	1.33226	1.33228	− .00013	75.	1.32442	1.32434	−0.00022
35.	1.33164	1.33157	− .00014	80.	1.32330	1.32323	−0.00023
40.	1.33093	1.33087	− .00015	85.	1.32215	1.32208	−0.00024
45.	1.33017	1.33011	− .00016	90.	1.32096	1.32086	−0.00025
50.	1.32934	1.32930	− .00017	95.	1.31971	1.31959	−0.00026
55	1.32847	1.32846	− .00018	100.	1.31843	1.31819	−0.00030

Kettler made observations for sodium light at nine different temperatures ranging from 20.9° to 95.17° C. inclusive. From these nine observations by extrapolation and interpolation he gives a table of values from − 10° to 200° C., from which table the values given above are taken. We now know that extrapolation from the range he used to the zero point is not justifiable owing to the rapidly decreasing numerical value of dn/dt as the freezing point is approached. Extrapolation is also not justifiable near the boiling point because of the rapidly increasing numerical value of dn/dt. This rapid increase in the numerical value of dn/dt as the boiling point is approached is probably due to the increasing quantities of water vapor in the water.

Empirical Formulas.—Numerous empirical formulas have been proposed connecting the index of refraction of water with the temperature. Dufet [1] proposes

$$n = n_0 - 10^{-7}(125.5t + 20.642t^2 - 0.00435t^3 - 0.00115t^4),$$

where n represents the refractive index at the temperature t° C., and n_0 the refractive index at 0° C. This formula was arrived at by setting up an empirical equation for dn/dt, from the best data available at that time in the range below 50°, and integrating. As tested by the writers the equation is not applicable to temperatures above 50° C. Walter's formula,

$$n = n_0 - 10^{-6}(12t + 2.05t^2 - 0.005t^3),$$

a modification of Dufet's formula, holds well over the range studied by Walter, that is, from 0° to 30° C. It does not hold for higher ranges. Owing to the relatively low values of dn/dt near the freezing point and the relatively high values near the boiling point a single simple equation covering the entire range from 0° to 100° cannot be expected to have a high accuracy over the entire range. The writers propose

$$n = 1.33401 - 10^{-7}(66t + 26.2t^2 - 0.1817t^3 + 0.000755t^4).$$

Walter's value for n_0, viz., 1.33401, is used. This equation was obtained by substituting in the general form, $n_0 - n = at + bt^2 + ct^3 + dt^4$, the values of n and t for four different temperatures and solving the four simultaneous equations for a, b, c, and d. This was done for four sets of equations, using different temperatures in the different sets and taking a mean of the values thus obtained. Some slight adjustments were then made by inspection and trial. The equation was tested at every five-

[1] Jour. de Physique, 4, 389, 1885.

degree point between 0° and 100°, and the maximum error was found to be at 75° where the deviation from the observed value is + 7 units in the fifth decimal place.

Osborn (loc. cit.) has given an empirical relation for the value of dn/dt which agrees very closely with experiment for the range 0° to 40° C. It is, however, not applicable above 50° C.

A number of empirical relations connecting the refractive index of a liquid with the density of the liquid have been proposed. Of these only two will be mentioned. Gladstone and Dale[1] have proposed the relation $(n - 1)/d = R$, where n is the index of refraction, d the density, and R a constant. Lorenz[2] proposed

$$\frac{n^2 - 1}{n^2 + 1} \cdot \frac{1}{d} = P, \text{ a constant.}$$

Table V. gives the values of R and P for water, the densities being taken from the sixth edition of the Smithsonian Tables.

TABLE V.

$t.$	$R.$	$P.$	$t.$	$R.$	$P.$	$t.$	$R.$	$P.$
15°...	0.33370	0.28030	50°..	0.33291	0.28030	90°.	0.33201	0.28079
20....	.33357	.28026	60...	.33276	.28043	95..	.33187	.28087
30....	.33336	.28023	70...	.33249	.28051	100..	.33163	.28088
40....	.33309	.28019	80...	.33221	.28063			

Getman and Wilson[3] give a few values between 15° and 40° C. for the refractive index and for R for water. Their values for the range studied are higher for the refractive index and R, and lower for dn/dt than those obtained by other observers, including the writers.

Ethyl Alcohol and Carbon Bisulphide.—A large number of determinations of the index of refraction of ethyl alcohol and carbon bisulphide have been made, but so far as the writers are aware no determinations have been made in the temperature ranges approaching the boiling points of either liquid. In connection with these liquids the second form of prism only, with automatic temperature control, was used. The same general procedure was followed and the same degree of accuracy reached as in the case of water. Here, however, the materials were not specially purified. Kahlbaum's ethyl alcohol, 99.8 per cent. absolute, and J. T. Baker and Co.'s carbon bisulphide were used. The analysis furnished by the makers for the carbon bisulphide was sp. gr. 1.27, N.V.M. 0.001 per cent., SO_2, H_2S, SO_3 none.

[1] Phil. Trans., 1858, p. 887.

[2] Wied. Ann., 11, 77, 1880.

[3] Amer. Chem. Jr., 40, 468, 1908.

Determinations were made of the index of refraction of ethyl alcohol for fifty different temperatures between the limits of 15° and 75° C. These represent a number of runs each taken throughout the temperature range, the observations extending over several months. The values obtained were plotted on a large scale from which plot the results given in Table VI. were taken.

TABLE VI.

Index of Refraction, Relative to Air, of Kahlbaum's Ethyl Alcohol, 99.8 Per Cent. Absolute, for Sodium Light.

t.	*n.*	*t.*	*n.*	*t.*	*n.*	*t.*	*n.*
14° C....	1.36290	30° C...	1.35639	46° C...	1.34969	62° C...	1.34279
16.....	1 36210	32.....	1.35557	48.....	1.34885	64.....	1.34189
18.....	1.36129	34.....	1.35474	50.....	1.34800	66.....	1.34096
20.....	1.36048	36.....	1.35390	52.....	1.34715	68.....	1.34004
22.....	1.35967	38.....	1.35306	54.....	1.34629	70.....	1.33912
24.....	1.35885	40.....	1.35222	56.....	1.34543	72.....	1.33820
26.....	1.35803	42.....	1.35138	58.....	1.34456	74.....	1.33728
28.....	1.35721	44.....	1.35054	60.....	1.34368	76.....	1.33626

Determinations were made of the index of refraction of carbon bisulphide at forty-three different temperatures between the limits of 15.95° and 44.7° C. These determinations represent many runs taken throughout the temperature range. These results were plotted and Table VII. made.

TABLE VII.

The Index of Refraction of Carbon Bisulphide, Relative to Air, for Sodium Light.

t.	*n.*	*t.*	*n.*	*t.*	*n.*	*t.*	*n.*
15° C....	1.62935	24° C...	1.62226	34° C...	1.61413	44° C...	1.60582
16.....	1.62858	26.....	1.62064	36.....	1.61247	45.....	1.60499
18.....	1.62704	28.....	1.61902	38.....	1.61080		
20.....	1.62546	30.....	1.61740	40.....	1.60914		
22.....	1.62387	32.....	1.61577	42.....	1.60748		

TABLE VIII.

Values of dn/dt for Ethyl Alcohol and Carbon Bisulphide.

Temperature.	Ethyl Alcohol.	Carbon Bisulphide.
15° C.....	−0.00040	−0.00077
25.....	− .00041	− .00081
35.....	− .00042	− .00082
45.....	− .00042	− .00083
55.....	− .00043	
65.....	− .00045	
75.....	− .00046	

If n represents the index of refraction at any temperature $t°$ C., and n' the index of refraction at 15° C., then as an empirical equation we may write

$$n = n' - 10^{-6}[a(t - 15) + b(t - 15)^2 + c(t - 15)^3].$$

For ethyl alcohol for the range 15° to 70° $n' = 1.36250$, $a = 404$, $b = 0.22$, $c = 0.0025$.

For carbon bisulphide for the range 15° to 45° $n' = 1.62935$, $a = 766$, $b = 2.56$, $c = -0.035$.

Andrews[1] has made determinations on the index of refraction of ethyl alcohol, giving great care to the purity of the alcohol. His value, which he believes correct to one unit in the fifth place, at 25° C., for sodium light is 1.359408. The writers' value at this temperature is 1.35844. The writers believe this difference in observed value of the index is due to the difference in purity. For carbon bisulphide at 20° C. and for sodium light Landolt-Bornstein Tabellen give 1.62772 as the mean of the values obtained by four observers. The writers' value is 1.62546. Again the only explanation that can be offered is the difference in purity of the material. While slight impurities will change the value of the index of refraction, it is hardly to be expected that they would produce a large change in the value of dn/dt and it is the change in the refractive index with the temperature, rather than the value of the index for pure material that is emphasized in the case of alcohol and carbon bisulphide.

UNIVERSITY OF CALIFORNIA,
DEPARTMENT OF PHYSICS.

[1] Amer. Chem. Soc. Jr., 30, 353, 1908.

MEASUREMENT OF MERCURY VAPOR PRESSURE BY MEANS OF THE KNUDSEN PRESSURE GAUGE.

BY CHARLES F. HILL.

SYNOPSIS.

Vapor Pressure of Mercury, 0 to 35° C.—The disagreement among the results obtained by previous observers for this range of temperature suggested the need for a *direct determination* of the vapor pressures *with a Knudsen gauge.* Impurities were eliminated by numerous distillations in a system cut off from the pump by a liquid air trap, and the slight amount of residual gas was corrected for. The readings obtained at 19 temperatures lie near a smooth curve which, it is believed, gives the vapor pressures to within 3 per cent. The values for 0, 10, 20, and 30° C. are, respectively, .000350, .000775, .00182 and .00407 mm. of Hg, considerably higher than those obtained by Knudsen in 1909, but agreeing fairly well with Morley's results up to 15°, and at higher temperatures with values extrapolated from the results of Ramsey and Young.

HISTORICAL.

WHILE engaged in experimental work in the spring of 1920, an accurate knowledge of the vapor pressure of mercury at room temperature became of importance. On looking for the values given in tables for temperatures below 40° C. very little agreement among the various observers was found as may be seen in the following table.

TABLE I.

T.	Regnault 1862.	Hagen 1882.	Hertz 1882.	Ramsey and Young 1886.	Van der Plaats 1886.	Morley 1904.	Knudsen 1909.
0°	.02	.015	.00019	——	.00047	.0004	.000184
10°	.0268	.018	.0005	——	.0008	.0008	.0005
20°	.0372	.021	.0013	——	.0013	.0015	.00188
30°	.053	.026	.0029	——	——	.003	.00278
40°	.0767	.033	.0063	.008	——	.006	.006
50°	.112	.042	.013	.015	——	.011	.0126
60°	——	——	——	——	——	.021	——
70°	——	——	——	——	——	.04	——

In 1886 van der Plaats[1] published results obtained by taking a large number of readings between 0 and 20° Centigrade. Values from his mean curve are usually given preference in tables. The method was to pass dry gas through water, through sulphuric acid, and then through mercury until saturated, after which the mercury was collected by gold and pumice stone and weighed. The vapor pressure was calculated from the data obtained by comparison with the vapor pressure of water.

[1] Rec. Trans. Chim., 5, p. 49, 1886.

Van der Plaats' readings show considerable variation, but are consistent enough so that with the number of readings taken his results must be given considerable weight. The method would not be expected to give values too high since his chief error should be loss of evaporated mercury.

E. W. Morley[1] in 1904 used practically the same method as van der Plaats except that the evaporated mercury was measured by weighing the sample before and after evaporation. Readings were taken at 16, 30, 40, 50, 60 and 70° C., and Dalton's equation

$$P = ab^t$$

was used for the calculation of the mean curve and for extrapolation to 0° C. Morley's readings at 40, 30 and 16° C., are from 8 to 20 per cent. below his mean curve but at the higher temperatures his values agree with those given by others. Vapor-pressure curves should have a decreasing per cent. increase as the temperature increases. Morley's curve is perfectly uniform if the slope is measured in this way, but the error in the readings at low temperatures could easily account for this fact. While Morley can not claim a high percentage accuracy his agreement with van der Plaats at low temperatures, and with the other observers at higher temperatures, seems to indicate that the order of his values is correct.

The last data of importance published were those of Knudsen[2] in 1909. An equation was developed for the flow of gas through a tube with a small opening over one end, and an apparatus based on this equation was arranged so that the vapor pressure of mercury could be measured. This equation

$$G = \sqrt{\frac{p' - p''}{W' + W''}} \times t$$

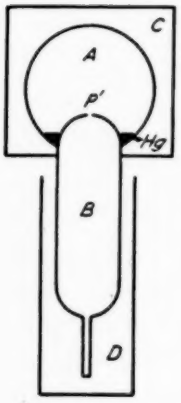

Fig. 1.

involves the pressure difference, the resistance of tube and opening, the density of the gas and the time. G is the mass of the gas or vapor which will flow through the small opening in an evacuated tube, as shown in Fig. 1, with a pressure difference $p' - p''$. In practice p'' was made zero by the application of a cold bath to B. Knudsen's results obtained by this method are about one half as large as those of Morley, and also of van der Plaats, in the region 0 to 40° C. The fact that mercury requires an appreciable time for evaporation might tend to produce such an effect since p' at the opening is being relieved continuously.

[1] Phil. Mag., Vol. –, p. 662, 1904.

[2] Ann. der Physik. 28, p. 75, 1908–9; ibid., 28, p. 999, 1908–9; ibid., 29, p. 179, 1909.

Experimental.

From the foregoing it seems desirable that there should be additional experimental data taken at ordinary working temperatures. The Knudsen pressure gauge, in the opinion of the writer, offered the most dependable method for such measurements since in its action it is independent of the nature of the gas, and also its range is approximately that of the vapor pressures to be measured. The Knudsen gauge available was not arranged to be used as an absolute manometer, but was calibrated by means of an accurately constructed McLeod gauge. The principle upon which the Knudsen[1] gauge depends is that the molecules of a residual gas in a partial vacuum are thrown off from a heated platinum foil, and striking a light and suitably suspended vane exert a couple, thus producing a deflection which may be read by means of an optical system. The deflection for zero pressure of course is zero. This fact makes it possible to use a McLeod gauge for calibration purposes, since calibration curves may be used with the origin as an accurately determined point. The McLeod gauge may be read quite accurately to .001 mm., or even less, provided the glass and mercury are kept clean.

A special pyrex glass McLeod gauge was constructed for the purpose and fused directly to the rest of the apparatus (including the Knudsen gauge) which was also of pyrex glass. The volume tube of the McLeod gauge was made comparatively large in order to lessen friction and surface-tension effects. The gauge was found to read consistently to .0005 mm. if the mercury and glass were kept clean. The apparatus was assembled as shown in Fig. 2. The Knudsen gauge A, and the sample

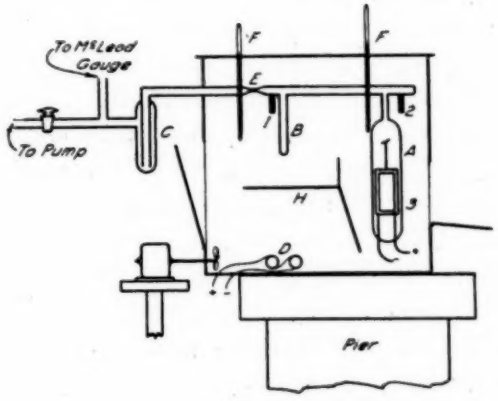

Fig. 2.

container B, were rigidly supported within a tight asbestos lined wooden box. The apparatus within the box was connected to the pumping

[1] Ann. der Physik, 32, pp. 809–842, 1910; Phys. Rev., 12, pp. 70–80, 1918.

system and McLeod gauge without through a tube of rather large diameter and including a mercury trap *C*. The system was evacuated by means of a Langmuir condensation pump supported by a Gaede rotary mercury pump. By continued pumping and with liquid air surrounding the trap *C* the pressure was readily brought down to about .005 mm. Hg. It was then further reduced by approximately equal steps. At each step the pressure as indicated by the McLeod gauge was accurately read simultaneously with the deflection of the Knudsen gauge, while a given constant current flowed through the platinum foil of the gauge. In this way data for a calibration curve were obtained. To test the consistency of the readings (for both gauges) sets of data were taken in which the current supplied to the gauge had in turn the values .3, .4, .5, .6 ampere. This data when plotted on 40 cm. coördinate paper gave, for each set, a smooth curve, showing that the two gauges were at least consistent.

The sample of mercury was then introduced into the container *B* and with liquid air surrounding the trap *C*, and the pumps running, the mercury was distilled slowly out of the container *B* and back again by heating first the container and then the rest of the tube. This process of distillation was carried out a number of times. Warm water was kept on the sample to prevent loss of the sample and condensation of vapors while the entire tube within the asbestos-lined box was heated to a temperature of 250 to 300° C. for several hours in order to drive the vapors out of the walls of the tube. The apparatus was then sealed off at *E*. After allowing the box to come to the desired temperature for a time, the total pressure was taken. The mercury was then driven into the container *B*, while submerged in liquid air, by warming the rest of the tube, and the residual gas pressure measured. The difference between the total and the residual pressures is the vapor pressure of the mercury. Readings were thus taken at a number of temperatures over the range 0 to 35°. After completing the series the tube was opened, resealed to the pump and the same process of distillation and heating carried out again. This method was continued until minimum values for the vapor pressure were obtained on three successive sets of readings. The mercury was considered pure at this point.

Another calibration of the Knudsen gauge was now carried out, a second sample of mercury, purified with nitric acid, was introduced and the process of distillation and heating was repeated eight times. The tube was then sealed off again at *E* and readings were taken at several different temperatures.

The four sets of data obtained in this way contained nineteen indi-

vidual values for the vapor pressure of mercury extending over the temperature interval of $-.7$ to $34.9°$ Centigrade. Of these values two or three differ from the mean curve by about 6 per cent., the rest being within 3 per cent. of the curve. In the following discussion it will be shown that this is about the accuracy that could be expected from the method.

The temperatures within the asbestos-lined box were read by means of two tenth-degree mercurial thermometers placed at different points. To insure uniform temperature the air was caused to circulate within the box by a fan driven by a motor without. The fan system was supported separately from the pier and box to prevent jarring the Knudsen gauge. The circulation of the air was directed by the bafflers *H*. Two heating coils, *D*, controlled the high temperatures, while the low temperatures were obtained by opening the windows and cooling the room. In general the temperatures were held constant, probably at .1 or very readily at .2° C. Changes of .2° in the box temperature produced changes in the vapor pressure that were just detectable by the Knudsen gauge. The gauge did not register changes as quickly as the thermometers. The Knudsen gauge was read by a lamp and scale at one meter distance. In order to hold the zero point, or rather to hold the vane and foil at a constant distance, the scale was rigidly fixed to the floor. If the vane became displaced, it could be brought back to its original position by merely restoring the zero on the scale. One set of calibration curves was used for three sets of data, and between each set the calibration was checked to make sure that it remained constant.

In order to determine the probable accuracy of the method some of the sources of error and their probable magnitude will now be considered. In the first place, impurities tend to increase the vapor pressure in the tube, so that this method would be expected to give values too high. The first sample gave minimum values for about eight distillations, and since the process of distillation was carried out more than twenty times, this error was considered eliminated. The second sample was first treated with nitric acid and then distilled eight times, hence we were justified in considering that the errors due to impurities in this sample were negligible. Special care was taken to keep the McLeod gauge and the mercury in it clean in order to prevent changes in friction. It was found that upon taking several readings at the same pressure the gauge could be read to within a total range of ± 2 per cent., except at the low pressures and these seemed to check well with the other readings as shown by the curves. The accurately known point on the curve at the origin helped to take care of this source of error. There was a

variation of 3 per cent. in the Knudsen gauge readings, however, if a new set of calibration curves were drawn through the same points, a variation would be obtained that would account for most of this error. Allowing for a probable error of ± 2 per cent. for temperature variations and the same for each of the other sources of error, the total probable error should be within about ± 6 per cent. The fact that this is the range of the actual readings seems to indicate that the principle sources of error have been accounted for and the data are about what one should expect from the method.

TABLE II.

Third Run of Data.

I.	R_0.	*R.*	Deflection.	Total Pressure from Curve.	Mean.	Temperature.
.3	9.8	13.0	3.2	.00277		
.4		15.3	5.5	.00274		25°
.5		18.0	8.2	.00276		
.6		20.9	11.1	.00272	.00275	
.3	10.0	14.32	4.32	.00432		
.4		17.3	7.3	.00438		30.8
.5		20.7	10.7	.00422		
.6		24.5	14.5	.00416	.00427	
.3	10.0	15.0	5.0	.0055		
.4		18.55	8.55	.00556		34.3
.5		22.5	12.5	.0054		
.6		26.75	16.75	.00514	.00540	
.3	9.7	11.05	1.35	.00087		
.4		12.02	2.32	.00088		
.5		13.19	3.49	.00089		11.6
.6		14.5	4.8	.00088	.00088	
.3	10.2	10.8	.6	.00033		
.4		11.17	.97	.00036		−.7
.5		11.7	1.5	.00036		
.6		12.35	2.15	.00036	.00035	
				Residual Pressure from Curve.		
.3	10.15		deflection hardly perceptible			
.4		10.19	.04	.00002		
.5		10.23	.08	.00002		
.6		10.28	.13	.00002	.00002	

One set of the actual readings taken is given in Table II. which constituted the third run in the first series. The total pressure for a given

temperature is given in the fifth column for different values of current flowing through the Knudsen gauge. The mean of these is recorded in the sixth column. At the bottom of the table is the data giving the residual gas pressure. Obviously the total pressure less this gas pressure is the vapor pressure of mercury. Table II. contains the data for the vapor pressure of mercury at five different temperatures. A second series, in which a new sample of mercury cleaned with nitric acid as noted earlier, gave values of the vapor pressure for additional temperatures. Together the two series gave nineteen values extending over a range in temperature from $-.7$ to 34.9° C. which are collected in Table III. The corresponding graph is shown in Fig. 3. The points

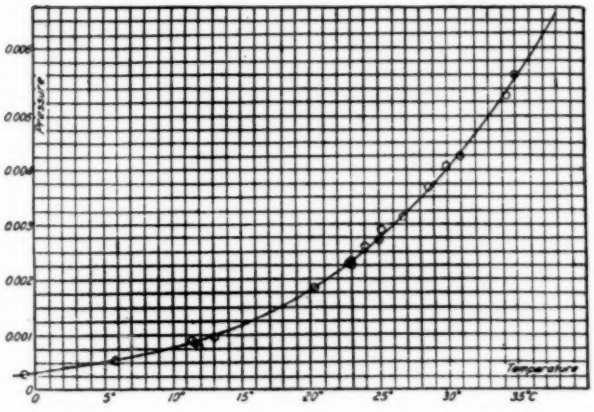

Fig. 3.

TABLE III.

Values for the Vapor Pressure of Mercury at Various Temperatures.

Temperature.	Pressure mm. Mercury.	Temperature.	Pressure mm. Mercury.
−.7°	.00033	24.0°	.00262
5.7	.00055	25.0	.00273
11.4	.00092	25.6	.00292
11.6	.00086	26.8	.003145
11.6	.000815	28.6	.0037
13.0	.00097	29.9	.004075
20.3	.00187	30.8	.00425
22.8	.00230	34.3	.00538
23.0	.00224	34.9	.00575
23.0	.00235		

all lie well upon a smooth curve. In Table IV. the vapor pressure of mercury in mm. is given for 2-degree intervals taken from the curve.

In conclusion, the author wishes to thank Professor A. P. Carman for the use of the facilities of the laboratory, and also to thank Professor

C. T. Knipp for the interest he has taken in the work and for the many suggestions offered.

TABLE IV.

Values for Each 2° as Taken from Smooth Curve Through the Points.

0.0°	.000350 mm. Hg.	22.0°	.00214 mm. Hg.
2.0	.000412	24.0	.00234
4.0	.000487	26.0	.003
6.0	.000572	28.0	.0035
8.0	.000662	30.0	.00407
10.0	.000775	32.0	.00467
12.0	.000895	34.0	.00535
14.0	.00105	36.0	.00607
16.0	.00126	38.0	.00695
18.0	.00150	40.0	.008
20.0	.00182		

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ON THE AGEING EFFECT IN THE MOBILITY OF POSITIVE GAS IONS.

BY H. B. WAHLIN.

SYNOPSIS.

Mobility of positive ions of air immediately after formation has been found by Erikson, using a modified Zeleny method, to be much higher than the normal value. This result has been verified by the author using the alternating potential method. Ions formed in an ante-chamber by α-rays from polonium were driven by a weak auxiliary field into the measuring chamber where the mobility was determined by the use of an alternating field of 1,800 to 3,600 cycles and of variable strength. Pure dry air was used at a pressure of 30 mm. When the auxiliary potential was 1.5 volts the measured mobility was normal but when the potential was 3.0 volts or more the mobility rose to 1.80 cm./sec./volt/cm., indicating that the ions entered the measuring chamber before they were aged. The time required for the ions to age or reach the normal condition is estimated to be between 1/75 and 1/120 of a second.

AT the November meeting of the American Physical Society, Professor H. A. Erikson, of the University of Minnesota, presented a paper on the variation in the mobility of positively charged gas ions with time. Using a modification of the Zeleny method for measuring mobilities Professor Erikson[1] has shown that if the determinations are made immediately after the ions are formed, the values obtained are for air, oxygen, and nitrogen much higher than the accepted values. If, however, the ions are aged for an appreciable time Erikson found this time to be of the order of 1/100 of a second (for air) before the determinations are made, the mobility falls to the normal value (1.37 cm. per sec. per volt per cm.).

In order to investigate this effect further, the writer constructed an apparatus on the principle of the Franck modification of the Rutherford alternating potential method for determining mobilities using α-particles from polonium as the ionizing source. As a source of alternating potential, an oscillating vacuum-tube circuit of the Hartley type (Fig. 1) with a telephone transformer (T) in the plate circuit was used. The voltage on the secondary of the transformer was varied by varying the potential of the plate by means of the potential dividing resistance R_2. In order to keep the frequency of the alternating potential constant with a variation in the plate voltage, a resistance (R_1) was introduced into the grid circuit of such a value that the potential could be varied over the desired range without any noticeable effect on the frequency.

[1] Erikson, PHYS. REV., 17, p. 400; 18, p. 100.

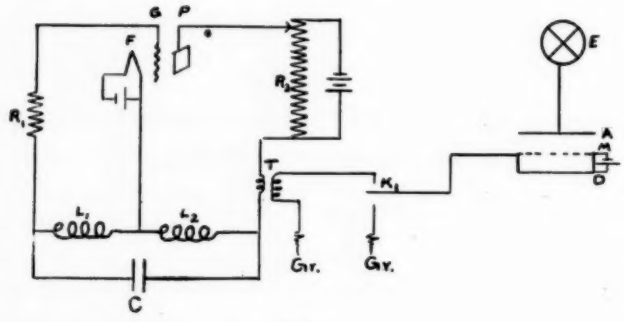

Fig. 1.

The inductances (L_1, L_2) and the capacity (C) were chosen so as to give a range of frequencies from 1,800 alternations per second to 3,600 alternations per second. One terminal of the secondary of the transformer was grounded, and the other was connected through a condenser key (K_1) to the gauze (M). On the lower side of this gauze a copper plate coated with polonium was fastened in such a manner that the radiation from the same was confined to the lower half of the region between M and D. The gauze was made by boring holes 1.3 mm. in diameter in a brass plate .5 mm. thick. The distance between centers of adjacent holes was 4 mm. The diameter of the gauze was 10 cm. This gauze was fastened to a fiber ring which rested on the brass plate (D). The distance between M and D was 1 cm. Between the gauze and the brass plate a source of potential was fastened for driving the ions through the gauze into the measuring field. A represents a collecting plate 10 cm. in diameter. The distance between A and M was varied between the limits of 6 mm. and 9 mm. The collecting plate in turn was connected through a platinum wire "bow switch" to the electrometer (E). The electrometer was of the Compton type with a gold sputtered quartz fiber as a suspension and was used at a sensibility of 4,500 scale divisions per volt with the scale at a distance of 150 cm. The amount of charge given to A in a given time was taken as a measure of the current. Then from the value of the alternating potential at which the ions cease to get across to the collecting plate the mobility may be calculated from the expression

$$K = \frac{\pi n d^2}{\sqrt{2}} \frac{P}{V\,760}, \qquad (1)$$

where K is the mobility at a pressure of 760 mm., P is the pressure, n the frequency, and V is the alternating potential.

In all these determinations air was used at pressures ranging from 1 cm. to 3 cm. of mercury. A number of mobility curves were obtained

at each pressure with values of the auxiliary field between M and D varying in some cases between 1.5 volts and 60 volts.

The air was purified by passing it over hot copper oxide to break up organic impurities. This would also remove the hydrogen. It next passed over potassium hydroxide to remove carbon dioxide and then through calcium chloride and phosphorous pentoxide to remove water vapor, and finally into the chamber containing the plates A, M and D. Before taking a series of readings, the chamber was washed out by exhausting to a pressure of 1 mm. or less and filling to atmospheric pressure. This was repeated three or four times, so that the residual gas left in the chamber from the previous filling was very small. In order to prevent any contamination of the gas by vapors from the walls of the chamber, the readings were taken immediately after making a filling. However, there was no noticeable difference produced in the results by allowing the gas to remain in the chamber for some time.

If the effect observed by Erikson is correct, we should expect that for low values of the auxiliary field between M and D, the ions would remain in this field long enough so that by the time they are carried through the gauze they will be aged, and that the intercept of the mobility curve on the voltage axis would give the normal value of the mobility. However, as the auxiliary field is increased ions would get through the gauze before ageing and the intercept would give values for the mobility which are abnormally high. As will be seen from Fig. 2, this is the case, for

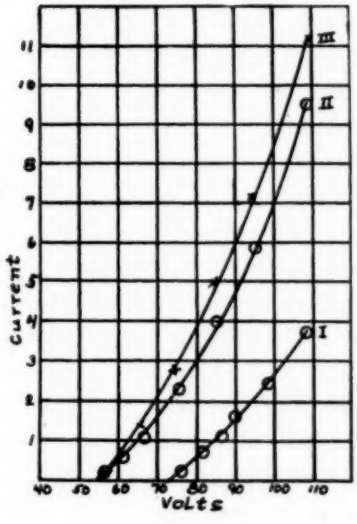

Fig. 2.

Frequency of alternating potential, 1,800 alternations per second. Plate distance d, 8 mm. Pressure of gas, 30 mm. Curve I., Auxiliary field, 1.5 volts. Curve II., Auxiliary field, 3.0 volts. Curve III., Auxiliary field, 4.5 volts.

with an auxiliary field of 1.5 volts the value for the mobility is 1.35 cm. per sec. per volt per cm., and with an auxiliary field of 3.0 volts the value rises to 1.80 cm. per sec. per volt per cm. A further increase in the auxiliary field does not change the intercept, as may be seen from the fact that the intercept for a field of 4.5 volts is the same as for 3.0 volts. The slight tendency shown by curve number 1 to be concaved upwards is probably due to the fact that the gauze and the collecting plate were not accurately parallel, for since the distance between these two is of the order of 8 mm. and since in the expression for the mobility constant (equation 1) this distance enters as the square, a small variation in this distance would produce quite an appreciable effect in altering the shape of the curve. The increased concavity of curves 2 and 3 is probably due to the fact that theions passing through the gauze are both the aged and unaged variety. The estimated time necessary for ageing is for all the curves taken somewhere between 1/75 and 1/120 of a second.

Discussion of Results.

Erikson has been unable to notice any ageing in the mobility of the negative ion. In this case, however, the effect is complicated by the fact that we have a distribution of mobilities between electronic and ionic. Determinations of the mobilities of the negative ions have shown that in most gases the mobility constant becomes abnormally high as the pressure is decreased. This would indicate that the electron does not attach itself immediately to a molecule but will travel some distance through a gas before uniting to form a negative ion. It would seem from this then that a further change after the electron once has attached itself is not very probable.

The most obvious explanation of the results given above is on the basis of a cluster theory of ion formation. On such a theory the formation of a positively charged gas ion would consist first in the detachment of an electron from the neutral molecule to form the positive ion and then the attachment of molecules to this ion to form the cluster. Then if the mobility is measured before this clustering takes place, the mean free path of the ion would be greater and as a consequence the mobility higher.

If, however, a cluster is formed, it is to be expected that it will disintegrate if the field in which the mobility is measured becomes high enough and the mobility will rise to a value limited principally by the size of the molecule or atom which forms the nucleus of the cluster. This question has been investigated by Loeb,[1] Chattock, Tyndall, and others without obtaining any evidence for an increase in the mobility.

[1] Loeb, PHYS. REV., December, 1916.

Wellisch, Franck, Franck and Meitner, and Rutherford have found that for a given gaseous medium the mobility is independent of the nature of the carrier as long as it is of atomic dimensions. On the basis of a small ion theory it is therefore to be expected that an aged ion would have the same mobility as an unaged one. However, these results can be coördinated on the basis of a cluster theory if the ions used by these observers were aged before the mobility was determined and if the size of the cluster is independent of the carrier which forms the nucleus.

In conclusion, the writer wishes to express his thanks to Mr. J. P. Foerst for his work in connection with the construction of the apparatus used in these determinations.

UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN.

THE EFFECT OF DISSOLVED SUBSTANCES ON THE DEPOSITION OF COLLOIDAL PARTICLES FROM A SOLUTION BY MEANS OF AN ELECTRIC CURRENT.

BY RICHARD D. KLEEMAN.

SYNOPSIS.

Effect of Various Dissolved Substances on Porcelain Slip (a Colloidal Solution of Particles of Clay, Flint, and Feldspar in Water).—(1) *Effect on compactness of deposit produced by an electric current.* It was found that the addition of only from 0.1 to 0.3 per cent. of any one of a number of substances, including Na_2SiO_3, Na_2SO_4, Na_3PO_4, Na_2HPO_4, H tartrate, Na tartrate, NaOH and KOH, resulted in a deposit which, though not quite dry, was solid instead of being semi-liquid. The compactness does not depend on the current density. As the amount of substance added is increased, the compactness increases less and less and soon reaches a limiting value. The full effect of the substance does not appear at once but only after a period which varies up to several hours. (2) *Effect on the fluidity of the slip* is to increase it markedly. From the relative action of different substances this effect is intimately related to the first one. Although the result of adding the substance is first to precipitate some of the particles, when more solid material is added the precipitate is redissolved so that for the same fluidity the proportion of solid dissolved is much greater with the added substance than without. (3) *Suggested explanation.* Both effects may be explained if we assume that the radii of the spheres of action of the particles of the slip are diminished by the dissolved substance. Particles will go into colloidal solution if no combinations result from encounters. This property is expressed in terms of the interfacial surface tension of the particles. *The equations of distribution of colloidal particles under the action of gravity* are obtained and with their help an explanation of the effect mentioned above, the precipitation and re-solution of the particles of the slip, is suggested. From a consideration of the experimental results it is concluded that the volume of the *spheres of action of a particle in porcelain slip* is about double the actual volume of the particle.

DURING some experiments on the electric deposition of porcelain slip it was observed that the deposit obtained from the slip used in the wet porcelain process (in which the slip is cast into molds of plaster of Paris) was solid though not quite dry, while that obtained from slip used in the dry process was of the consistency of thick cream. It was soon found that the difference in the nature of the deposits obtained was due to the small quantity of sodium silicate (Na_2SiO_3) that is mixed with the slip used in the wet process. Porcelain slip, it should be mentioned, consists of a colloidal solution of particles of clay, flint, and feldspar, in water. A systematic investigation was next carried out with the assistance of Mr. Chase to determine the effect of various dissolved substances on the nature of the deposit obtained. It was found that besides sodium silicate the substances Na_2SO_4, Na_3PO_4,

Na_2HPO_4, H tartrate, Na tartrate, NaOH, KOH showed the effect very well, and in fact it was found that most substances showed the effect in a more or less degree.

The hardness or compactness of the deposit obtained increased with the amount of substance added. It was difficult, from the nature of things, to obtain definite quantitative results. It may, however, be remarked that in a general way the compactness of the deposit appeared to increase at first rapidly with the amount of substance added, and gradually less so till a point was reached beyond which further addition of the substance did not produce any appreciable effect, the relation between amount of substance added and compactness of deposit obtained thus resembles a saturation curve. The minimum amount of substance necessary to add in order to produce the maximum compactness was usually very small, it was difficult to determine exactly in any given case for reasons that follow from the preceding remarks. The order of the quantity is 1 part in 300–1,000 by weight. The full effect of the substance added does not appear at once, but after a time which may vary from a quarter of an hour to several hours. Stirring seems to help the final state being reached more rapidly.

The compactness of the deposit obtained with slip containing one of the substances mentioned did not seem to depend on the density of the current used, provided that it was not so large that the gases evolved interfered with the deposition. Very small current densities were occasionally used, of the order of a milliampere and less, so that it was necessary to let the current flow for hours to obtain a deposit a quarter of an inch thick, but the compactness of the solid deposit obtained did not seem to be different from that obtained with larger currents. Scarcely any transition layer seemed to exist between the deposit and the slip, whatever the current density, and a short exposure of the deposit to the air was therefore sufficient to dry its surface. This effect was specially noticeable when sodium silicate was added to the slip.

The increase in compactness of the deposit, obtained on the addition to the slip of one of the substances mentioned, was found to be intimately connected with the increase in fluidity of the slip which was found to be produced by these substances. The connection between the two effects may be well illustrated by the following typical experiment. Suppose that a deposit is obtained electrically from pure slip containing about 30 per cent. of solid matter by weight. The deposit will be of the consistency of thick cream. Now let a small quantity of Na_3PO_4, about one part in three hundred by weight, be added. This will give rise to a partial precipitation of the particles of the slip, the flint and feldspar

particles mainly being affected. But this precipitate goes into solution again on adding additional solid matter. Now we may go on adding solid matter till a point is reached when the fluidity of the slip is the same as that it possessed before the addition of Na_3PO_4. It will then contain about 60 per cent. of solid matter by weight, or about double the amount it possessed initially. The amount of solid added may be taken as a measure of the increase in fluidity produced by the dissolved substance. The deposit obtained from the slip will now be in a solid instead of in a semi-liquid state. Similarly the connection between the two effects may be traced in the case of other substances, and for different amounts of a substance added. It was found that an increase in the compactness of the deposit, as far as such a thing could be judged, was attended by an increase in the fluidity of the slip as measured in the foregoing manner, or by the rate of its flow.

The relation between the two effects may be very simply and strikingly explained by assuming that the addition of a small amount of a substance to the slip decreases the radii of the spheres of action of the particles, or the spheres associated with the particles which do not penetrate into each other during their motion of translation. The particles would then pack more closely on being deposited by an electric current, and the fluidity of the solution would be increased since the particles would possess more freedom of motion with respect to each other.

We may obtain some information about the sphere of action of a particle from increase of fluidity considerations. The addition of a small quantity of Na_3PO_4 of one part in three hundred by weight to the slip, we have seen, necessitates doubling the amount of solid matter in order to keep the fluidity constant. It may be taken as a first approximation that the total volume of the spheres of action of the particles in the slip was not changed during the process. It would then follow that the volume of the sphere of action of a particle in the slip was decreased to half its value through the addition of the Na_3PO_4, and that the volume of the former sphere of action is, therefore, greater than twice the volume of the particle. This appears to be borne out by experiments on the amount of water content in the deposit from *pure slip* by an electric current, which was found to be about one half of the total volume of the deposit. Experiments with clay alone gave in this manner a value of about two thirds, or a ratio of 3 to 1 of the total volume of the spheres of action of the particles to their actual volume.

If a small quantity of Na_3PO_4, about one part in three hundred by weight, is added to porcelain slip containing about 30 per cent. of solid matter, some of the particles are immediately precipitated and then a

gradual process of precipitation goes on. On adding more solid matter and agitating the solution the precipitated particles may be brought into solution again and kept suspended. The experiment first of all shows that the radii of the spheres of action of the particles were decreased to about the actual volume of the particles by the addition of the Na_3PO_4. This is supported by the fact that the deposit obtained by an electric current is solid. The experiment also shows that the ability of particles to keep in suspension in a solution may depend on their number. A theoretical investigation of this point is given further on.

It will be of interest to point out in this connection that particles of flint and feldspar do not by themselves go into colloidal solution in water, but clay particles do, and that therefore in porcelain slip the flint and feldspar particles are kept in suspension in the solution by the clay particles.

We may now proceed to consider some theoretical aspects of the foregoing experiments, and of colloidal solutions in general. The condition that particles mixed with a liquid may remain in colloidal solution is that two particles on colliding should separate again, or that apparent forces of repulsion should come into play when two particles approach each other. These forces, it will be shown, may be expressed in terms of the interfacial surface tension of the particles in contact with the solvent. The surface tension of a liquid in contact with a solid is the external work done in separating two pieces of the substance in close contact submerged in the liquid per unit area of the surface of contact. The surface work of a particle is accordingly equal to the area of its surface multiplied by its interfacial surface tension. Hence when two particles approach one another in a liquid this would be attended by a change in their total surface work. If this increases, the corresponding external work is done by the particles at the expense of their kinetic energy, the effect being as if forces of repulsion were called into play on approach of the particles. Therefore if ΔW_s denote the increase in the surface work of two particles approaching one another, they will separate again if

$$\Delta W_s \geqq E,$$

where E denotes the kinetic energy of the particles. If the surface work W_s, or the interfacial surface tension is negative, which corresponds to external work being done by the system on producing additional interfacial surface, ΔW_s corresponds to a numerical decrease in W_s, while if ΔW_s is positive, or the surface tension is positive, W_s corresponds to a numerical increase in W_s. Therefore if the interfacial

surface tension of the particles is positive, and two particles do not combine on collision, it follows that the formation of new interfacial surface would in the initial part of the process require the expenditure of external work, or apparent forces of attraction would come into play, while during the remaining part of the process the system would do work, or apparent forces of repulsion would come into play. These forces of repulsion prevent the particles from uniting, but it is evident that if by any chance the particles came into contact under the foregoing conditions, they would remain in contact. If however the interfacial surface tension is negative, the particles would separate again if brought into actual contact.

The area of the change in the transition surface for a given distance of approach of two equal colloidal particles would evidently on the average be proportional to the cube root of the mass of one of the particles, and the force of repulsion would increase in proportion. Hence if the kinetic energy of each particle were proportional to the absolute temperature, as is the case with a molecule in the gaseous state, and thus independent of its mass, the distance of approach of the particles would be the less the greater their masses. Hence under these conditions the chance of two particles combining would be the smaller the greater their masses. But the kinetic energy of a colloidal particle is not likely to be proportional to the temperature, nor at any temperature equal to that of a molecule in the gaseous state, as has been pointed out by the writer.[1] At present it is impossible therefore to say how the chance of combination of two particles depends on their size.

The boundary between a solid and liquid in contact we would expect to be the seat of a liquid transition layer. The density of the liquid in the layer would accordingly undergo a gradual change from one side to the other, and this may be attended by a separation of electrical charges. The work done in the production of the electrical layers, it should be noted, is *included* in the *interfacial surface tension*. In a separate paper under the title "A Transition or Adsorption Layer Theory of the E.M.F. of a Voltaic Cell," the nature and properties of this transition layer are discussed. The forces called into play on encounter of two colloidal particles are obviously in part directly due to the separated electrical charges of opposite sign associated with their transition layers. Thus the outside electrical layers of two particles of the same kind have the same sign, and forces of repulsion will therefore initially come into play on approach of the particles.

[1] A Kinetic Theory of Gases and Liquids, by R. D. Kleeman, pp. 210–217, John Wiley & Sons, New York.

The distribution of the particles in a solution under the action of gravity is of importance to consider in this connection. The differential equation of equilibrium is

$$F \cdot \delta h = \delta P_s,$$

where P_s denotes the osmotic pressure of the particles at a distance h from the surface of the solution, and F the force due to gravity acting on the particles in a cubic cm. of the solution. If v_a denotes the volume of a particle, ρ_a its density, ρ the density of the liquid, we have

$$F = gv_a(\rho_a - \rho)N_c,$$

where N_c denotes the concentration of the particles. If the solution is dilute, the osmotic pressure of the particles obeys the gas laws, or

$$P_s = \frac{RT}{N} N_c,$$

where N denotes the number of molecules in a gram molecule. The equation of equilibrium may accordingly be written

$$mgN_c \cdot \delta h = \frac{RT}{N} \cdot \delta N_c, \tag{1}$$

substituting m for $v_a(\rho_a - \rho)$ the apparent mass of a particle. On integrating this equation we obtain

$$mgh = \frac{RT}{N} \log \frac{N_c''}{N_c'}, \tag{2}$$

where N_c' denotes the concentration of the particles in the surface of the solution, and N_c'' that at a distance h from the surface.

The foregoing concentrations may conveniently be expressed in terms of N_h the total number of particles in a cylinder of unit cross-section and height h. We have directly

$$\int_0^h N_c \cdot \delta h = N_h,$$

an equation which on being transformed by the help of equation (1) and integrated gives

$$N_c'' - N_c' = N_h \frac{Ngm}{RT}. \tag{3}$$

From this equation and equation (2) we obtain

$$N_c'(e^{\frac{Nmgh}{RT}} - 1) = \frac{N_h Ngm}{RT} \tag{4}$$

and

$$N_c''(e^{\frac{Nmgh}{RT}} - 1) = \frac{N_h Ngm}{RT} e^{\frac{Nmgh}{RT}}. \tag{5}$$

It appears from equation (2) that the ratio of the concentration of the particles corresponding to the upper surface and bottom of a solution is independent of the total number of particles provided their masses are kept the same. Therefore if a sufficiently large number of colloidal particles are added to a solution, the concentration of the particles at the bottom of the solution as given by equation (2) may be greater than that corresponding to the particles being in contact with each other. A layer of precipitated particles will accordingly form at the bottom of the vessel. But these particles will not differ from those in solution, and will readily go into solution again on adding a sufficient amount of liquid. The particles in the (apparent) precipitate would however not pack so closely as would be the case if they were dry, but their centers of mass would be separated by distances approximately equal to the diameter of their spheres of action when in solution. These considerations indicate another method for obtaining values of the radii of the spheres of action of colloidal particles in a solution.

We have seen that particles which do not go into colloidal solution by themselves may be induced to do so on adding particles that readily form a colloidal solution. An explanation of this may now be given. The *complete* precipitation of the particles from a solution means first of all that the particles gradually increase in size through combination. This gives rise to a gradual increase in concentration of the particles at the bottom of the vessel in comparison with that in the surface of the solution, according to equation (2). Ultimately a precipitate will be formed in the way already explained. Finally practically no particles will be in solution on account of their size. Hence if particles which by themselves readily go into solution keep in suspension particles which by themselves do not go into solution, the following state of affairs probably exists. A particle of the former kind on encountering one of the latter will not combine with it, since the former particle has a sphere of action associated with it extending into the liquid. If however, two particles of the latter kind encounter each other they would combine. But they may separate again in time through encounters with other particles, the chance of that happening depending on the number of other particles present. Thus the presence of particles which unaided remain in solution might have the effect of keeping the complexity of aggregations of particles of the other kind below a certain average degree, and thus prevent a precipitation of the latter particles. The effectiveness of this will evidently depend on the relative concentrations of the two different kinds of particles, and the total concentration of the particles. The fact mentioned that the flint and feldspar particles

of porcelain slip are more or less kept in suspension by the clay particles, and that a precipitate obtained on adding a substance may be made to go into solution again through the addition of particles, are well explained in this way.

General Electric Co.,
Schenectady, N. Y.

THE HALL, ETTINGSHAUSEN, NERNST AND LEDUC EFFECTS IN CADMIUM, NICKEL AND ZINC.

BY A. E. CASWELL.

SYNOPSIS.

Transverse Magnetic Effects in Cadmium, Nickel and Zinc.—The Hall, Ettingshausen, Nernst and Leduc effects were all measured for each metal on the same thin strip, which after being provided with various thermocouples and potential wires was heated electrically in vacuum and placed in a magnetic field of 4,000 to 5,200 gauss. Coefficients are given for cadmium (40 to 50°), nickel (− 11 to 57°) and zinc (− 25 to 77°). The Hall and Ettingshausen effects were not found of opposite sign as has usually been observed, but both came out positive.

SINCE the thermoelectric, galvanomagnetic and thermomagnetic effects observed in metals have not been determined for the same specimens and since these properties vary considerably in different specimens of the same substance the writer undertook to construct an apparatus with which to measure the transverse magnetic effects and the thermoelectric effects in the same specimen over a wide range of temperatures. So far he has been unable to determine the thermoelectric effects, especially the Thomson, with any degree of accuracy for any specimen sufficiently thin to give satisfactory results for the magnetic effects.

A considerable part of the work has been done under the auspices of the National Research Council in the Palmer Physical Laboratory of Princeton University. The writer takes pleasure in acknowledging his indebtedness to Dean Magie, who very kindly placed all the resources of the Laboratory at his disposal, and in expressing his deep appreciation of the uniform courtesy and generous coöperation shown him by all the members of the Princeton staff.

In the following paragraphs the most reliable results obtained for the transverse mangetic effects are given, being comparable in accuracy with the better results published elsewhere. Moreover, the published data are somewhat meager.

The specimens used were rolled to a uniform thickness of 0.01035 cm. from sticks of Kahlbaum's c. p. reagent cadmium, and of Kahlbaum's c. p. I zinc, and sheets of c. p. nickel. They were 1.2 cm. in breadth and 4.2 cm. in length, being firmly held at the ends by copper clamps through which the primary currents of electricity and heat were led into and out of the specimens. Four copper-constantan thermocouples were

attached at intervals of 1.2 cm. along the longitudinal axis of the specimen, and two others were attached at the centers of its upper and lower edges. By means of these the temperatures of different points on the specimen were determined, the copper wires of the thermocouples being also used to determine electric potential differences. The thermo-elements were used with a potentiometer reading to one-twentieth of a microvolt, the galvanometer being a Leeds-Northrup High Sensitivity Type R. The specimen, together with its clamps, was placed within an evacuated tube connecting two flasks of the Dewar type in which liquids could be placed with which to maintain steady temperature conditions. The tube was placed between the poles of a large Pye electromagnet by means of which fields were produced ranging from about 4000 to 5200 gauss.

In order to reduce the loss of heat through the thermocouples these were made of No. 44 copper and No. 34 constantan wire.

The results obtained are collected in Table I; R, P, Q and S being, respectively, the coefficients of the Hall, Ettingshausen, Nernst and Leduc effects. The Hall coefficient is defined by the equation $E = R(HI/D)$, where H is the intensity of the magnetic field in gausses, I is the primary electric current through the specimen in amperes, D is the thickness of the specimen in cm., and E is the resulting electric difference in potential between the two edges expressed in volts. Similarly, the Ettingshausen coefficient is given by the equation $T = P(HI/D)$, where T is the resulting temperature difference between the edges expressed in degrees Centigrade. The coefficient of the Nernst effect is given by $E = QHB(dt/dx)$, where B is the breadth of the specimen in cm. and dt/dx is the primary temperature gradient. The coefficient of the Leduc effect is given by $T = SHB(dt/dx)$, the symbols having the same significance as before. The sign of these effects is taken as positive when, the magnetic field being directed away from the observer and the primary current of heat or electricity flowing from left to right, the upper edge of the specimen is at the higher temperature or potential.

TABLE I.

Hall Effect.		Ettingshausen Effect.		Nernst Effect.		Leduc Effect.	
Temp. °C.	$R \times 10^{13}$.	Temp. C.	$P \times 10^{8}$.	Temp. °C.	$Q \times 10^{12}$.	Temp. °C.	$S \times 10^{7}$.
				Cadmium.			
+42.0	+ 8.50	+51.2	+5.96	+39.4	0	+39.4	− 1.87
+49.3	+ 11.67						

Nickel.

+57.2	+770.7	+55.8	+3.67	−11.4 +37.6	+ 8.36 + 27.47	−11.8 +38.9	0 −10.17

Zinc.

−24.7	+ 15.33	−17.1	0	−16.2	+290.0	−16.2	+37.59
+25.5	+ 8.20	+45.2	+1.76	+37.2	− 6.25	+37.2	+ 4.00
+32.6	+ 8.38	+60.7	+2.27				
+39.9	+ 8.18	+76.7	+3.02				
+41.2	+ 8.23						
+76.7	+ 9.82						

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